



JOURNAL  
OF  
THE CHEMICAL SOCIETY.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
BRITISH AND FOREIGN JOURNALS.

PART II.

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General and Physical Chemistry.

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**Influence of Ultra-red Characteristic Frequencies on the Coefficient of Refractivity in the Visible Portions of the Spectrum.** J. WYNNER (*Physikal. Zeitsch.*, 1918, 19, 483—486).

—A mathematical paper, in which it is shown that the relationship, which may be deduced from the Drude theory and the work of Dehlinger, may be used to calculate the influence of the ultra-red characteristic frequencies on the refractive index in the visible region. Further, the relationship gives a picture of the nature of the vibrations to which the characteristic frequencies are due. Corresponding with the  $k$  relationship for solids with two atoms or atomic groups in the molecule, a similar  $k$  relationship may be deduced by analogous methods for liquid substances with three atomic groups as origin of the ultra-red characteristic frequencies. In the case of monohydric alcohols, it is shown that in the ultra-red absorption spectrum the wave-lengths of the superposed harmonic absorption region are related as the roots of the masses of the vibrating atomic groups.

J. F. S.

**Origin of Spectra.** J. C. McLENNAN (*Proc. Physical Soc., London*, 1918, 31, 1—29).—The Guthrie lecture, in which the modern views of spectroscopy are discussed along with the methods of determination of spectra in the extreme ultra-violet. J. F. S.

**Fundamental Frequencies in the Spectra of Various Elements.** J. C. McLENNAN and H. J. C. IRETON (*Phil. Mag.*, 1918, [vi], 36, 461—471).—It is shown that when zinc and cad-



with the second order spectrum. The intensity of the lines is indicated, as also is the presence of doublets, reversed lines, and broadened lines.

J. F. S.

**The Arc Spectrum of Zirconium, Measured in Terms of the International Normal.** W. VAHLE (*Zeitsch. wiss. Photochem.*, 1918, 18, 84—137).—The arc spectrum of zirconium has been measured by means of a concave Rowland grating 6.34 metres in diameter and ruled with 787 lines per mm. Zirconium nitrate was vaporised in a carbon arc and the spectrum photographed. Long lists of the lines measured are given over the range  $2285.229\ \mu\mu$ — $7169.044\ \mu\mu$ , and these are compared with the measurements of Bachem. An accuracy exceeding  $0.005\ \mu\mu$  is claimed for the stronger lines. The measurements were made with the second order spectrum for wave-lengths below  $5658\ \mu\mu$  and with the first order spectrum for larger wave-lengths.

J. F. S.

**Absorption Spectra of some Derivatives of cycloPropane.** EMMA P. CARR and C. PAULINE BURT (*J. Amer. Chem. Soc.*, 1918, 40, 1590—1600).—In order to investigate further the effect of ring-formation on absorption spectra, the authors have examined a number of cyclopropane derivatives, their ethylenic isomerides, and the corresponding open-chain compounds. The series includes (1) methyl  $\gamma$ -benzoyl- $\beta$ -phenylethylmalonate, methyl 3-benzoyl-2-phenylcyclopropanedicarboxylate, and the two isomeric methyl  $\beta$ -benzoyl- $\gamma$ -phenylvinylmalonates; (2) methyl anisoylphenylethylmalonate, methyl 3-anisoyl-2-phenylcyclopropanedicarboxylate, and the two isomeric methyl  $\beta$ -anisoyl- $\gamma$ -phenylvinylmalonates; (3) methyl benzoylphenylpropylmalonate and the isomeric methyl benzoyl-2-phenyl-3-methylcyclopropanedicarboxylates; (4)  $\alpha$ - $\gamma$ -dibenzoyl- $\beta$ -phenylpropane, 1:3-dibenzoyl-2-phenylcyclopropane, and 1:3-dibenzoyl-2-phenylcyclopropene. (For preparation of these compounds, see Kohler and Conant, A., 1917, i, 566, 568.)

The authors find that the character of the absorption is closely related to the form of linking of the three central carbon atoms, and distinct differences in the absorption spectra of the corresponding cyclic, open-chain, saturated, and olefinic compounds are shown. In each series the cyclic substance shows an absorption quite similar to that of its open-chain analogue, but in every case the general absorption is greater. Evidently closure of the ring increases the absorptive power of the molecule.

Ring-formation in the cyclopropanes causes a shifting of the absorption towards the visible end, but to a less extent than in the case of the isomeric ethylenic compounds. These facts justify the conclusion that the cyclopropane ring is a centre of residual affinity similar in character, but intermediate in quantity to that of the double linking, and as such can form a conjugated system with a carbonyl group in the proper position.

The absorption spectra of four pairs of geometrical isomerides have been determined; in each pair the isomeride of lower m. p.



gave slightly greater general absorption and the isomeride of higher m. p. the greater tendency toward selective absorption. H. W.

**Influence of Substituents of Reactions. III. Influence of Substituents on the Colour of Benzene Picrate.** HARTWIG FRANZEN (*J. pr. Chem.*, 1918, [ii], 98, 67—80).—The problem has been previously investigated in a series of experiments on the rate of reduction of substituted phenylhydrazines (A., 1918, i, 456); as data can only be slowly accumulated in this manner, the author has sought a more convenient method, and has examined the absorption spectra of a series of picrates of benzene and its derivatives. He is led to the following conclusions: A relationship exists between the influence of a substituent of the first order on the rate of reduction of phenylhydrazine and on the colour of benzene picrate; a substituent which increases the rate of reduction of the hydrazine deepens the colour of the picrate. The activity of the substituent depends on the degree of unsaturation of the atom united to the ring carbon atom; depth of colour increases with the degree of unsaturation. If the latter is decreased by introduction of another atom, the colour becomes brighter. Among the picrates of benzene derivatives with substituents of the first order, the meta-compounds are always the least and the para-compounds the most intensely coloured; ortho-compounds occupy an intermediate position, and are only slightly darker than the meta-compounds.

H. W.

**Phenomena of Luminescence in Pyrazoline Derivatives.** FRITZ STRAUS [with CARL MUFFAT and W. HEITZ] (*Ber.*, 1918, 51, 1457—1477).—See this vol., i, 41.

**Chemiluminescence.** I. LIFSCHITZ (*Helv. Chim. Acta*, 1918, 1, 472—474).—A preliminary account of work which is not yet completed.

Organomagnesium compounds of the type  $\text{RMgX}$  are very suitable for the study of chemiluminescence. Moeller (*Arch. Pharmaci Chemi*, 1914) has shown that the phenomenon only occurs with aromatic substances. It is now found that the difference between the aromatic and aliphatic compounds depends on the relative stability of the etherates; all ether-free Grignard reagents emit light in the presence of oxygen or nitrous oxide, but not of nitric oxide, nitrogen peroxide, carbon dioxide, and water. The additive compounds of organomagnesium substances with dimethylaniline are faintly luminescent in oxygen, but only in the case of aromatic derivatives.

The thermochemistry of the gradual addition of ether to suspensions of Grignard's reagents in benzene has been studied. With aliphatic reagents the greatest development of heat occurs when the first two molecules of ether are added, and very little heat is developed after the addition of four molecules; with aromatic reagents, on the other hand, the greater part of the heat is not

developed until four molecules of ether have been added, and further addition produces a still considerable effect. H. W.

#### Light Scattered by Gases ; its Polarisation and Intensity.

THE HON. R. J. STRUTT (*Proc. Roy. Soc.*, 1918, [A], 95, 155—176).—The light scattered at right angles by gases and vapours is not completely polarised. The vibrations parallel to the existing beam have always an appreciable intensity, which in ordinary cases varies from 1.2% (pentane) to 14% (nitrous oxide) of the intensity in the perpendicular direction. Helium is an outstanding case, polarising far less completely than any other gas. The measurements give an intensity in the parallel component nearly half as great as that in the perpendicular component. Theory indicates that this is the ratio to be expected if vibration in the helium atom is limited to a direction fixed within the atom, on the assumption of random orientation to the exciting light. Such an atom is the antithesis of the spherical atom or molecule which would give perfect polarisation. The intensity of scattering by the different gases tried varies as the square of the refractivity, within the limits of experimental error. Saturated vapours, even when very dense, show no increase of scattering power beyond what is expected from the density. If molecular aggregates are formed they are not numerous enough to show by this method. Liquid ether apparently scatters about even times less light than a corresponding mass of ether vapour.

J. F. S.

#### Rotation Dispersion and Inversion of *l*-Menthone.

BERNARD GROSSMANN and KURT BRAUER (*J. pr. Chem.*, 1918, [iii], 8, 9—66).—The rotation dispersion of *l*-menthone has been determined for a large number of solvents at 20°; the specific rotation for  $c=5$  varied from  $-13^\circ$  to  $-25^\circ$ , and from  $-35^\circ$  to  $-60^\circ$  in red and violet light respectively. The dispersion-coefficient,  $[\alpha]_D/[\alpha]_V$ , lay between 2.16 and 2.80. Certain *d*-menthones have been obtained by inversion of *l*-menthone by concentrated sulphuric acid, according to Beckmann's method; determination of their dispersion-coefficients proves that they are not optical antipodes of *l*-menthone.

The rotation dispersion of *l*-menthone after being boiled with organic acids has been investigated in the actual solutions, which were found to be dextrorotatory, and the observations have been confirmed by examining the rotation dispersions of the menthones separated from such solutions either by water or by distillation. The values of  $[\alpha]_D/[\alpha]_V$  lay between 3.12 and 3.67 for the solution and between 3.25 and 3.68 for the separated menthone. *l*-Menthone remains levorotatory after being boiled with acetic anhydride; the dispersion-coefficient of the dissolved and separated menthone is abnormally low (1.73 and 2.01 respectively).

*l*-Menthone exhibits mutarotation when dissolved in formic acid or bromoform; the inversion in concentrated sulphuric acid solution

has been polarimetrically examined, and mutarotation has been observed.

The rotation-dispersion of *l*-menthone in alcoholic potassium hydroxide and hydrochloric acid solution has been investigated; the rotation is immediately positive, and is unchanged by heating. The value  $[\alpha]_D/[\alpha]_T$  is unusually high, amounting to 4.35 or 3.87 for solutions and 5.07 or 5.57 for the separated menthones. When *d*-menthone is dissolved in alcoholic potassium hydroxide, the rotation falls noticeably, thus differing from its behaviour in formic and sulphuric acids, in which the rotation remains constant.

The gradual inversion of *l*-menthone at its boiling point has been investigated by a study of the rotation dispersion. An instance of abnormal rotation dispersion is here encountered, and the occurrence of a definite end-point, which is not altered by protracted heating, is established. The same end-point is reached more rapidly if *d*-menthone is used as initial material. The dispersion-coefficients at first decrease, then increase, and become infinitely great at zero, and subsequently sink until the value 3.47 is obtained; this value is exhibited by the so-called *d*-menthone.

The optical behaviour of *d*-menthones has been examined in a number of solvents; the specific rotation is found to be invariably increased in solution, whilst that of *l*-menthone is depressed. The dispersion-coefficients varied from 3.13 to 3.26.

The intra-molecular transformation suffered by *l*-menthone when heated appears to depend on desmotropy, equilibrium between the ketonic and enolic forms being slightly attained.

Inversion of *l*-menthone by various solvents is attributed to the additive or substitutive action of the latter, and the formation of *d*-menthone is due to a type of Walden inversion, this substance being formed by decomposition of intermediate products which are probably only stable in solution.

The influence of solvents on the specific rotation of optically active substances is due to reactions occurring between solvent and solute, for which the alteration in rotation is a particularly sensitive indicator.

H. W.

**Law of Blackening of Layers Sensitive to Light.** F. HALLA and A. SCHULLER (*Zeitsch. physikal. Chem.*, 1918, **93**, 173—182).—In a previous paper (*Zeitsch. wiss. Photochem.*, 1912, **11**) a relationship was put forward between the depth to which a film sensitive to light is darkened by light and the time of exposure. The relationships are now exactly and mathematically formulated. The calculations are extended to the case where the film lies on a reflecting base. The scattering of light is insufficient to explain the peculiarities observed in the blackening curves. The reflection of the base is shown to change, not only the depth of the blackening, but also the definition of the picture.

J. F. S.

**The Radioactive Properties of the Mineral Springs of Colorado.** O. C. LESTER (*Amer. J. Sci.*, 1918, [iv], **46**, 621—637).—The emanation content of more than 100 spring waters from Colorado

has been measured, and also the radioactivity of numerous samples of spring deposits. A high average activity of the waters was found, the most active examined showing the highest activity of any in the United States and surpassed only by a few foreign springs. For five springs the emanation content exceeded 100 (curies  $\times 10^{-10}$  per litre), the highest being 305, and ninety-five springs exceeded 10. Of the latter, 75% were in or near metamorphic and igneous formations, but some of the most active were in sedimentaries. Thorium emanation was detected in only one spring. No springs of extraordinarily high emanation content were found, and although radioactive ores are abundant there are no large springs found near them. The measurements were for the most part carried out in the field by boiling out the water by Boltwood's method. F. S.

**Thorium-Lead.** KASIMIR FAJANS, F. RICHTER, and (FRL.) J. RAUCHENBERGER (*Sitzungsber. Heidelberger Akad. Wiss.*, 1918, pp. 28; from *Chem. Zentr.*, 1918, ii, 438—439).—According to theory, in addition to ordinary lead, there must be at least two members of the lead series with different atomic weights; on the one hand, radium-G or radium-lead, the final product of the uranium-radium series with an atomic weight 205.94, and, on the other, thorium-lead (Th-D), the atomic weight of which is calculated from that of thorium to be 208.08. Radium-G would be expected to occur in uranium minerals free from thorium, whilst thorium-lead must be looked for in thorium minerals free from uranium. The problem of isolating the latter is rendered difficult by the fact that thorium minerals free from uranium do not exist, whilst those poor in uranium are scarce. A mineral is unsuitable for investigation if it does not contain at least 4—5 times as much thorium as uranium, provided that thorium-lead and uranium-lead are either completely stable elements or have an approximately equal life period. The lead content of certain thorium minerals appears to point to the conclusion, however, that thorium-lead is relatively unstable, thus adding to the difficulty of its isolation.

The authors have examined a sample of thorite containing 30–10% of thorium, 0.44–0.45% of uranium, 0.35% of lead, in addition to unestimated amounts of silica, iron, rare earths, and traces of bismuth. The mineral was treated with fuming hydrochloric acid in glass flasks, in which decomposition is effected far more rapidly than in porcelain dishes. The solution was evaporated to dryness and the silica removed. Before precipitation of lead with hydrogen sulphide, the ferric iron was reduced to the ferrous state by means of hydroxylamine, and subsequent operations were conducted in an inert atmosphere. The lead was precipitated as sulphide, and converted first into the chloride and then into the sulphate, of which 4 grams were obtained. The mean of three analyses (performed by Hönigschmid) gave as atomic weight  $207.90 \pm 0.013$ . On the supposition that uranium-lead and thorium-lead are perfectly stable elements, the whole of the lead separated from the thorite taken should have an atomic weight lying between the limits 207.97 and

208.00 if the atomic weight of thorium is taken as 232.12, that of helium as 4.00, and that of thorium-lead as 208.08. When the slight experimental and theoretical uncertainties are taken into consideration, the agreement between the practical (207.90) and theoretical (208.00) values may be regarded as satisfactory, and there is therefore no good reason for supposing that thorium-lead is not a stable element. If the slight discrepancy is actual, it is probably to be explained by the presence of ordinary lead (atomic weight 207.2); if, however, it is to be ascribed to the instability of thorium-lead, the lower limit for the half period of the element regarded as a uniform material is calculated to be  $1.7 \times 10^8$  years. In any case, the existence of thorium-lead, obtainable in weighable amount and with an atomic weight approximating to 208.0, is placed beyond doubt.

H. W.

**Electrochemical Behaviour of Metals.** A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **21**, 158—171).—A theoretical paper, in which the relationships and equilibria between metal atoms, ions, and electrons are considered in the case of attackable metals (zinc) and non-attackable metals (nickel). These relationships are considered with regard to the potential difference between the metals and solutions of their ions and to the action of acids on the metals. In the first place, the consideration deals with equilibrium and velocity of the changes, both being considered in connexion with the Nernst solution theory, and in the second place the relationships are dealt with on the basis of the phase rule,  $\Delta z$  diagrams being evolved for the case of zinc and nickel as representing attackable and non-attackable electrodes.

J. F. S.

**Passivity of Chromium. III.** A. H. W. ATEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **21**, 138—150. Compare A., 1918, ii, 183, 193).—A theoretical paper, in which the reasons for the activation of passive chromium by cathodic polarisation are discussed.

J. F. S.

**Activation of Carbon Monoxide by Metallic Copper, the Generator Gas-cell and the Electromotive Activation of Alkali Formates.** K. A. HOFMANN (*Ber.*, 1918, **51**, 1526—1537).—The author's discovery (this vol., ii, 23) that carbon monoxide in the presence of oxygen is rapidly oxidised to carbon dioxide at the ordinary temperature at a copper surface moistened with an alkali hydroxide has enabled him to realise the generator gas-cell,  $O_2|Cu|alkali|Cu|CO$ , and the drawbacks common to most of such cells have been overcome (subject of a censored patent). The *E.M.F.* ( $CO \rightarrow CO_2$ ) is found to be 1.32 volts at  $20^\circ$ , which compares well with the value 1.343 volts at  $17^\circ$ , calculated by Nernst and von Warburg from the dissociation of carbon dioxide. The present paper deals with the purely scientific aspect of the problem. It is shown that the activation of the carbon monoxide is not due to the formation of an alkali formate. The suggestion is made that

a labile isoformate,  $\text{OH}\cdot\text{C}\cdot\text{OK}$ , is produced; its formation is only minimal at the ordinary temperature when carbon monoxide and an alkali alone are present, but is stimulated in the presence of copper.  
C. S.

**Dissociation of Strong Electrolytes.** NIELS BJERRUM (*Zeitsch. Elektrochem.*, 1918, **24**, 321—328).—A theoretical paper, wherein an hypothesis is developed according to which the strong electrolytes are completely dissociated. Because of the electrical forces between the ions, these electrolytes exhibit decreasing osmotic pressure, conductivity, and activity with increasing ion concentration. These decreases can be expressed by means of three numerical coefficients. A thermodynamic relationship between the activity and osmotic coefficients is developed and an approximate formula for the activity coefficient is worked out. The activity-coefficient possesses considerable chemical interest, and methods are outlined by means of which it may be determined, and in this connexion it is shown that the so-called neutral salt action, the anomalies of strong electrolytes, and the catalytic action of undissociated molecules only occur because the conductivity-coefficient has been used in calculations where more accurately the activity-coefficient should have been employed.  
J. F. S.

**Ionic Migration in Liquid Crystals of Hydrated Ammonium Oleate.** O. LEHMANN (*Ann. Physik.*, 1918, [iv], **57**, 244—256).—The changes effected in the appearance of liquid crystals of hydrated ammonium oleate under potential differences of 0—100 volts have been studied microscopically and with the aid of crossed nicols. The liquid crystal was contained in a capillary of 0.06 cm. diameter, and contact made with two platinum electrodes by means of a drop of ammonia solution saturated with ammonium chloride. The appearance at the electrodes, using various potentials, is described, and it is shown that the main cause of the observed phenomena is the re-formation of the hydrate of ammonium oleate from the ions which have migrated from the tube, and the taking up of these by the molecules present.  
J. F. S.

**Mechanism of Cathodic Metal Separation.** V. KOHLSCHÜTTER and E. VUILLEUMIER (*Zeitsch. Elektrochem.*, 1918, **24**, 300—321).—The electrolytic deposition of nickel from various solutions and under a series of different conditions has been studied with the object of finding an experimental connexion between the chemical polarisation and the form of electrolytically deposited metals. To ascertain this, the characteristic internal tension, which electrolytic nickel possesses, was investigated by depositing the metal on a platinum sheet and following the bending of the sheet. By this means it is shown that from the first moment the deposit undergoes a contraction which increases with further deposition. Consequently two processes must occur successively: first the formation of a film on the cathode, followed by a contraction of the film.

When the nickel is dissolved from such a contracted cathode the metal of the cathode returns to its original form. Consequently, the amount of bending corresponds with an equilibrium position, and the observation of the bending with time under stated conditions leads to characteristic curves. The process is dependent on the current density, and the composition of the electrolyte. It is strongly influenced by the addition of other substances to the electrolyte, and is less in solutions which cause an evolution of hydrogen, and also when the deposit is fine grained. When an already bent cathode is charged with hydrogen it straightens out again, but if the current is interrupted at this stage, the hydrogen is set free and the cathode takes up its original bent form. In solutions which do not evolve hydrogen the contraction occurs in jumps, which have the characteristics of delayed effects. The whole effect probably is due to the fact that the metal is at first deposited in a highly disperse form, and then the particles sinter with the formation of a denser material. This probably occurs along with the formation of a gas layer on the cathode, which plays the part of a dispersion medium. Since the electrolytic solution pressure of the highly disperse form is necessarily greater than that of the denser metal, this view explains the increase in the deposition potential above that of the ordinary metal.

J. F. S.

#### The "Curie Point" of Pure Iron and Ferrosilicon.

A. SANFOURCHE (*Compt. rend.*, 1918, **167**, 683—865).—It was shown by Curie that at about 1280° the magnetic property of iron was suddenly increased, in the ratio of about 3 to 2, and he termed this state of iron between 1280° and its melting point,  $\delta$ . Pure iron prepared by the author melted at 1515°, and when slowly cooled its magnetic property suddenly changed at 1310°, whilst, on re-heating the iron, the break in the curve occurred at 1365°. This critical point is the "Curie point,"  $A_4$ . The temperature at which it is shown is rapidly, though slightly, lowered by the addition of silicon in amounts up to 1% (1281°); above that amount the magnetic change is smaller, and with amounts of silicon in excess of 2.5% (1195°) is no longer perceptible.

C. A. M.

**A Relation between Boiling Points at One Atmosphere and in a "Vacuum."** W. P. JORISSEN (*Zeitsch. anorg. Chem.*, 1918, **104**, 157—162).—Since the critical temperature of any substance is approximately equal to twice the boiling temperature (absolute) in a vacuum (20 mm.) and to 1.55 times the boiling temperature at atmospheric pressure, it follows that the ratio of the two boiling temperatures,  $T_{(20 \text{ mm.})}/T_{(1 \text{ atm.})}$  is a constant, equal to 0.78. This ratio is shown to be constant for a large number of substances, both organic and inorganic. The constancy of the ratio can be deduced from van der Waals's vapour pressure formula and from the results of a number of independent workers.

E. H. R.

**Latent Heat of Fusion as the Energy of Molecular Rotation.**KÔTARÔ HONDA (*Sci. Rep. Tohoku. Imp. Univ.*, 1918, 7, 123—130).

—A theoretical paper, in which the author develops the equation  $w\lambda/T_m = nE_{rm}/2T_m$ , in which  $T_m$  is the melting point in absolute degrees,  $E$  is the molecular energy belonging to each degree of freedom of the molecules, and  $n=2$  or 3. This equation is tested by evaluating both sides and comparing the results for a number of elements. The equation is based on the assumption that during melting very little energy is required for internal or external work, and the numerical results show that for elements of group I this assumption is fully justified. In the case of a second group of elements which includes bismuth, tin, iodine, gallium, bromine, and chlorine, the values of  $w\lambda/T_m$  are much greater than those for  $nE_{rm}/2T_m$ . In the case of compounds, agreement between the two sides of the equation can be obtained if  $n$  is taken as larger than 2, that is, if the molecules have more than two degrees of freedom for rotation. This implies that compounds have a molecular structure both in the liquid and solid states.

J. F. S.

**The Course of the Values of  $\alpha$  and  $b$  for Hydrogen at Different Temperatures and Volumes. III. and IV.**J. J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, 21, 1—15, 16—25. Compare A., 1918, ii, 185, 291).

—Theoretical papers, III. continuing the discussion of the pressure-volume relations in relation to the variability of  $\alpha$  and  $b$ , whilst in IV. the value of  $\alpha$  below the limiting temperature is discussed. A series of mathematical addenda to the previous papers are added.

J. F. S.

**Relationships between Absolute Temperatures and the Corresponding Absolute Pressures of Moist Vapours.**O. VENATOR (*Zeitsch. physikal. Chem.*, 1918, 93, 242—244).

—A short, critical discussion of the van der Waals's equation and its corollaries. It is shown that the value of  $\alpha$  is a variable one, having minima at the absolute zero and at the critical temperature, and increasing to a maximum as the temperature is raised or lowered respectively.

J. F. S.

**Raoul Pictet's Equation of Condition for Moist Vapours.**O. VENATOR (*Zeitsch. physikal. Chem.*, 1918, 93, 245—246. See

preceding abstract).—A criticism of Pictet's equation of condition for moist vapours. It is shown that this equation may be expressed in the form of the van der Waals's equation, and further that neither of these equations supplies the needs of the physico-chemical technology.

J. F. S.

**Relationship between Absolute Temperature and Absolute Pressure in Kilograms per Square Cm. for Moist Vapours.**O. VENATOR (*Zeitsch. physikal. Chem.*, 1918, 93, 247—249. See

preceding abstracts).—The author deduces from the van der Waals's



equation the expression  $\alpha = (T_k/T - 1)/(\log p_k - \log p)$ , in which  $T_k$  is the absolute critical temperature,  $p_k$  the corresponding pressure in kg./sq. cm.,  $T$  any temperature between  $T_k$  and the absolute zero,  $p$  the pressure corresponding with  $T$ . J. F. S.

**Negative Adsorption.** L. BERCZELLER (*Biochem. Zeitsch.*, 1918, **90**, 290—293).—Negative adsorption was observed in experiments with starch as adsorbent with both lactose and maltose. With coagulated albumin, negative adsorption was observed with dextrose, lactose, maltose, and sucrose. S. B. S.

**Dissociation of Salicylic Acid.** R. ORTHNER (*Zeitsch. physikal. Chem.*, 1918, **93**, 220—235).—Salicylic acid, when heated at 200° under pressures of from 10 cm. to 120 cm. of mercury is dissociated into phenol and carbon dioxide to the extent of 98—82%. The decrease in dissociation with pressure is shown to be in accord with the law of mass action. J. F. S.

**Reversal of the Dissociation of Salicylic Acid.** R. ORTHNER (*Zeitsch. physikal. Chem.*, 1918, **93**, 236—239. See preceding abstract).—The dissociation of salicylic acid at 200° has been measured at various pressures of phenol and carbon dioxide. It is shown that just as the dissociation of salicylic acid follows the law of mass action, so the reversal of the dissociation by these substances is strictly in keeping with the requirements of the mass action law. J. F. S.

[Dissociation of Salicylic Acid.] EMIL BAUR (*Zeitsch. physikal. Chem.*, 1918, **93**, 240—241. See preceding abstracts).—A theoretical explanation of some of the points arising out of the previous papers. J. F. S.

**Thickness of the Capillary Layer of Carbonic Acid.** G. BAKKER (*Zeitsch. physikal. Chem.*, 1918, **93**, 154—172).—A theoretical paper, in which methods of calculating the thickness of the capillary layer are deduced. These methods are then applied to the case of carbon dioxide. Making use of formulæ previously published (A., 1916, ii, 553), the equation  $\epsilon = -A/(v + \beta) + f(t)$  is deduced for calculating the energy of the homogeneous phases. In this equation  $A$  represents an arbitrary temperature function. The equation is arrived at by neglecting a small factor of a general equation, and a correction to compensate for this is applied to the resulting energy value. From the same original formula the value of  $\zeta$ , the thickness of the capillary layer, is calculated from the equation  $-4T[d(H/\zeta T)/dt] = (\rho_1 - \rho_2)r_1 + 2\{\epsilon_3 - (\epsilon_1 + \epsilon_2)/2\}(\rho_1 + \rho_2)^2$ ; this equation may be integrated and the integration constant evaluated, since  $H/\zeta T = 0$  at the critical temperature. A third method of calculating the thickness of the capillary layer is afforded by means of the equation  $\zeta = H/(p_s - p_r)$  where  $p_s$  is the vapour pressure and  $p_r$  the pressure in the long direction of the capillary layer.

As mean values for carbon dioxide, by all three methods, the following are obtained for  $\zeta$ :

$\lambda$ .....	-30°.	-10°.	0°.	10°.	20°.	25°.	30°.
$\zeta$ .....	1.46	1.72	1.91	2.21	3.51	7.06	26.1 $\mu$

The differences between the values calculated by the different methods do not constitute an objection to the present theory, but are due to the differences of the equation of condition used.

J. F. S.

**The Diffusion of Electrolytes into Jellies. I. The Relationship between the Distance of Diffusion and the Concentration.** OTTO VON FÜRTH and FRANZ BUBANOVIĆ (*Biochem. Zeitsch.*, 1918, **90**, 265—287).—Chlorides were allowed to diffuse into gelatin jellies containing silver nitrate, and the rate of diffusion could thus be measured by the silver chloride precipitate. If  $d$  = the distance of diffusion and  $k$  = concentration, it was found that after a time  $t$ ,  $d = mt^1/k^n$ , where  $m$  and  $n$  are constants. The constants vary with the properties of the jellies.  $n$  has the same value for the same jelly when different electrolytes are used. It has been found to vary between 0.10 and 0.31.

S. B. S.

**Dialysers made from Colloidal Membranes.** L. BERCZELLER (*Biochem. Zeitsch.*, 1918, **90**, 302—304).—Some remarks on the adsorption of iodine by collodion membranes, and the alteration of the permeability of the membranes according to whether they are treated with water when the organic solvent is still in them or they are nearly freed therefrom.

S. B. S.

**Colloid Chemistry and its Industrial Application.** F. G. DONNAN, W. C. McC. LEWIS, E. F. ARMSTRONG, and A. S. SHORTER (*Rep. Brit. Assoc.*, 1917, 20—105).—The first report of the committee appointed to compile information regarding the advances made in capillary and colloid chemistry with special reference to industrial processes. The various branches of the subject have been dealt with by specialists, and the following are included in the report: (1) viscosity of colloids, 3 pp., Emil Hatschek; (2) colloid chemistry of tanning, 15 pp., H. R. Procter; (3) general review and bibliography of dyeing, 19 pp., P. E. King; (4) colloid chemistry in the fermentation industries, 3 pp., Adrian J. Brown; (5) caoutchouc, 5 pp., Henry P. Stevens; (6) colloid chemistry of starch, gums, hemicelluloses, albumin, casein, gluten, and gelatin, 32 pp., H. B. Stocks; (7) colloids in the setting and hardening of cements, 4 pp., C. H. Desch; (8) nitrocellulose explosives from the point of view of colloidal chemistry, 2 pp., E. R. Chrystall; (9) celluloid from the standpoint of colloidal chemistry, 2 pp., E. R. Chrystall. Very full bibliographies are included in each of the sections.

J. F. S.

**Influence of Filtration on Hydrosols.** TADEUSZ MALARSKI (*Kolloid Zeitsch.*, 1918, **23**, 113—122).—The effect of filtration on

hydrosols of ferric hydroxide and silver, both alone and in the presence of electrolytes, has been determined by measuring the rate of motion towards the electrodes in an electric field. The experiments show that filtration, through filter-paper, fat-free cotton, glass wool, and sand has a very marked effect on the rate of motion of positive hydrosols and also on negative hydrosols the charge of which has been reduced or changed by the addition of electrolytes. This phenomenon is explainable by the theory of contact electrification. By successive filtration of ferric hydroxide sol through filter-paper, the potential difference of the double layer is diminished, and consequently the velocity in an electric field is also diminished; repeated filtration will reduce the potential difference to zero and finally change the sign of the charge. Solutions of silver which have been treated with aluminium sulphate so that macroscopic particles are visible on filtration become stable for weeks. This is to be explained by the retention of the aluminium ion by the filter-paper.

J. F. S.

**Spontaneous Transformation to a Colloid State of Solutions of Odorous Substances by Exposure to Ultra-violet Light.** H. ZWAARDEMAKER and F. HOGEWIND (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **21**, 131—137).—A number of solutions of odorous substances in water, glycerol, or paraffin are found after keeping for several weeks to have passed into the colloidal condition. The action is much more rapid in daylight than in the dark, whilst in the presence of ultra-violet light the action is still more rapid; in the case of many substances the transformation only occurs in the presence of ultra-violet light. The colloid particles are shown to be negatively charged. Among the substances examined, the following in decreasing order show a marked Tyndall cone: (1) in water solution: eugenol, cresol, guaiacol, carvacrol, citral, cumidine, thymol, and hypnone; (2) in glycerol solution: eugenol, safrole, cresol, nitrobenzene, and apiole; (3) in paraffin solution: aniline, eugenol, and cumidine.

J. F. S.

**Amphoteric Colloids. I. Chemical Influence of Hydrogen-ion Concentration.** J. LOEB (*J. Gen. Physiol.*, 1918, **1**, 39—60; from *Physiol. Abstr.*, 1918, **3**, 406).—At its isoelectric point, gelatin is undissociated. In acid solution, it forms cations only; in alkaline solutions, anions only. On the acid side of the isoelectric point, amphoteric colloids can combine only with anions of neutral salts; on the alkaline side, only with cations. At the isoelectric point, an amphoteric colloid cannot combine with either the cation or the anion of a neutral salt.

H. W. B.

**Inversion of Sucrose by Colloidal Silicic Acid.** ALBERT MARY and ALEXANDRE MARY (*Compt. rend.*, 1918, **167**, 644—646).—Colloidal silicic acid, prepared by the action of hydro-

chloric acid on sodium silicate solutions and subsequent dialysis, hydrolyses sucrose fairly rapidly. The activity of the dialysed solutions begins to diminish after a period depending on the concentration of the colloid; 8% solutions retain their full activity for five to six hours, and 1.5% solutions for several months. Feeble hydrolysing power is exhibited also by solutions which have not been dialysed, but rendered faintly alkaline with sodium hydrogen carbonate solution; for these solutions there is an optimal temperature below  $100^{\circ}$ , varying according to the conditions, such as concentration of electrolytes. Coagulation of such solutions, whether spontaneous or accelerated by heating, is associated with loss of hydrolytic activity. If non-dialysed solutions are rendered faintly alkaline with sodium silicate solution instead of sodium hydrogen carbonate, they show a higher inverting power, and heating neither produces coagulation nor destroys their activity.

The conclusion is drawn that hydrolytic activity is a function of the degree of dispersion of the colloid, and that rise in temperature increases the activity (as in the case of acid hydrolysis), but eventually produces changes in the degree of dispersion, culminating in coagulation, which set a limit to the increase. The optimal temperature observed in inversion by colloidal metals and by invertase is probably to be accounted for on similar lines.

J. H. L.

**Equilibrium between Carbon Monoxide, Carbon Dioxide, Sulphur Dioxide, and Free Sulphur.** J. B. FERGUSSON (*J. Amer. Chem. Soc.*, 1918, **40**, 1626—1644, 1900).—The reaction  $\text{CO} + \frac{1}{2}\text{SO}_2 \rightleftharpoons \text{CO}_2 + \frac{1}{2}\text{S}_2$  has been studied, and the equilibrium constants at  $1000^{\circ}$  and  $1200^{\circ}$  have been determined. The experiments were made by the "stream" and "semi-stream" methods both with and without contact substances. As contact substances, broken porcelain and platinised porcelain were used. It is shown that in all probability small quantities of carbonyl sulphide are also formed. The experimental data have been used to calculate the thermodynamic constants of the reaction and the free energy equations of this reaction, and also of the formation of sulphur dioxide from its elements.

J. F. S.

**Influence of Substitution in the Components of Binary Solutions Equilibria. XII. Binary Solutions Equilibria between Acid Amides and Phenols and their Derivatives.** ROBERT KREMANN and ALOIS AUER (*Monatsh.*, 1918, **39**, 441—493).—Fusion and solidification curves have been prepared for the following binary mixtures: (1) acetamide with the three nitrophenols, (2) benzamide with the three nitrophenols, (3) acetamide and salicylic acid, (4) benzamide and the three hydroxybenzoic acids, (5) acetamide and the three dihydroxybenzenes, and (6) benzamide with the three dihydroxybenzenes. Acetamide and *o*-nitrophenol form no compounds, but a simple eutectic at  $41.2^{\circ}$  with ca. 5% of acetamide. Acetamide forms compounds with equi-

molecular quantities of both *m*- and *p*-nitrophenol, which melt at 51.5° and 96.1° respectively. Benzamide and *o*-nitrophenol form no compounds, but a simple eutectic, m. p. 41.8°, with 5% benzamide. Benzamide and *p*-nitrophenol form an equimolecular compound, m. p. 97.2°. Acetamide and salicylic acid form a compound in the proportion of two molecules of the former to one of the latter, m. p. 108°, and a further compound in equimolecular quantities, m. p. 116°. Benzamide and *p*-hydroxybenzoic acid form a compound in equimolecular proportions, and also one with three molecules of benzamide to one molecule of *p*-hydroxybenzoic acid. Acetamide and quinol form an equimolecular compound, m. p. 101°; resorcinol and acetamide form a compound with two molecules of the latter to one of the former compound, m. p. 37.5°. Benzamide and quinol form a compound of two molecules of the former to one of the latter, m. p. 103.8; an equimolecular compound, m. p. 88.1°, is formed between resorcinol and benzamide.

J. F. S.

**Formation and Decomposition of Phloroglucinolcarboxylic Acid.** G. PIAZZA (*Zeitsch. physikal. Chem.*, 1918, 93, 183—219).—The equilibrium constant of the decomposition of the potassium salt of phloroglucinolcarboxylic acid, according to the equation  $C_6H_2(OH)_3 \cdot CO_2K + H_2O \rightleftharpoons KHC O_3 + C_6H_3(OH)_3$ , has been determined by titration with standard acid, using fluorescein as indicator, and taking as the end of the titration that point at which the fluorescence just disappeared. The velocity of formation and decomposition of potassium phloroglucinolcarboxylic acid has been determined at 50°. The course of the reaction was followed by the refraction of a beam of light, and was observed by means of a Löwe's interferometer. The velocity of decomposition was also followed by titration and by electrical conductivity measurements. Contrary to the usually observed behaviour, it is shown that the formation occurs much more slowly than the decomposition.

J. F. S.

**The Inflammation of Mixtures of Methane and Air in a Closed Vessel.** RICHARD VERNON WHEELER (*T.*, 1918, 113, 840—859).

**Hydrolysis of Ethyl Acetate by Alcoholic Sodium Hydroxide.** RUD. WEGSCHEIDER and (FRL.) LILLY RIPPER (*Monatsh.*, 1918, 39, 325—373).—The hydrolysis of ethyl acetate by solutions of sodium hydroxide in alcohol has been studied at 25°. The hydrolysis occurs according to the equation  $dx/dt = [\text{ester}][NaOH](0.12911(1-\alpha) + 0.05710\alpha)$ , in which  $\alpha$  is the degree of dissociation of the base calculated from the dissociation constant. The undissociated molecules of the base hydrolyse more rapidly than the ions. If all the products remain in solution, the reaction follows the equation for second-order reactions, but with a concentration of sodium hydroxide above 0.38, the reaction takes

place more rapidly than the equation demands. The addition of sodium acetate increases the velocity of the hydrolysis. This depends on the total sodium concentration of the solution. The falling off of the velocity, which, according to the theory, ought to take place on account of the precipitation of sodium acetate, is so small as to be unrecognisable in this case. With increasing water concentration, the velocity increases very rapidly. If the sodium hydroxide solution is prepared by adding sodium to the alcohol, and the water content is so small that the whole of the sodium is not converted into hydroxide, then the velocity is very small and the reaction does not occur according to the equation for reactions of the second order. This is probably because the hydrolysis is effected by the sodium hydroxide, and not by the sodium ethoxide. When sodium hydroxide is dissolved in concentrated methylated spirit, a considerable contraction occurs. Experiments on the water content to determine the equilibrium conditions between alcohol, sodium acetate, and its trihydrate at 25° led to no definite result, but point to the fact that a water content of 4–5% is necessary.

J. F. S.

**The Relative Activity of certain Alkyl Iodides with Sodium  $\alpha$ -Naphthoxide in Methyl Alcohol.** HENRY EDWARD COX (T., 1918, 113, 821–824).

**Preparation of Catalytically Active Substances.** FRIEDA MÜLLER (D.R.-P. 307380; from *Chem. Zentr.*, 1918, ii, 492–493).

Werner's salts [that is, the double salts of the heavy metals and complex salts described by Werner (*Neuere Anschauungen auf dem Gebiete der organischen Chemie*, 1913)] are heated with exclusion of air at a temperature not exceeding that at which the catalyst is intended to be used. Heating may occur in a current of nitrogen or in a vacuum; if the product is to be used as catalyst for reaction between gases, the heating may take place in an atmosphere of one or all of the gases. Previous to heating, the substance may be distributed over carriers, such as clay or asbestos. For reactions between liquids and gases, the heating may proceed in the liquid after the salt has been dissolved, suspended, or emulsified. In many cases, it is necessary to heat under pressure. A catalyst from potassium chromicyanide at 300° gave 15% of ammonia at 300° and 120 atmospheres. Ammonia undergoes quantitative combustion in the presence of the product from luteo-chromium ferricyanide at 300°. Ammonium ferrimolybdate when heated at 400° in an atmosphere of nitrogen and hydrogen yields a loose, black powder which yields 19% of ammonia at 160 atm. and 400°. Ammonium sodium cobalticyanide is converted by ignition at 700° in nitrogen into a very porous, black catalyst for the synthesis of ammonia. Carbonatopentamminecobalt nitrate is heated at 420° in a current of nitrogen and hydrogen for the preparation of a catalyst. Up to 8% of formaldehyde could be

obtained from methane and oxygen at  $150^{\circ}$  by use of a catalyst from croceocobalt nitrate (heated in nitrogen at  $150^{\circ}$ ). The catalyst from nitratopurpureocobalt nitrate is useful in the synthesis of ammonia. Indole is formed by hydrogenation of methyl *o*-toluidine in the presence of the catalyst from hexaquochromi-acetate. Borneol is converted into camphor in the presence of a product from hexaquochromi-propionate. A catalyst from cobalt hydroxynitrite brings about the quantitative oxidation of sulphur dioxide to sulphur trioxide by an excess of oxygen.

H. W.

**Hydrogenation and Dehydrogenation of Carbon Compounds with the Aid of Catalysts.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 307580, 307989; from *Chem. Zentr.*, 1918, ii, 573, 693).—The conversion of organic compounds or of oxides of carbon into hydrogenated substances can be effected at relatively very low temperatures if contact agents are used which, in addition to the catalysing metal (metals of the platinum-palladium group are excepted), contain oxides of the earth metals, including the rare earths or of glucinum or magnesium. Satisfactory activation can only be secured by the use of very intimate mixtures. These may be prepared by simultaneous precipitation of the suitable hydroxides, oxides, carbonates, etc., from a solution of mixed salts, by heating mixtures of molten salts, and also, though not always with equal certainty and effect, by mechanical processes, such as very fine grinding, kneading in the moist state, pressing, etc.; when necessary, the mass is subjected to subsequent ignition and reduction. The production of highly active contact agents is greatly facilitated if at any rate the catalysing metal is formed from salts containing carbon, such as carbonates, formates, etc. The activity of the contact agent is frequently increased by adding compounds of the alkali metals, for example, sodium hydroxide, either to the mixture itself or to the materials from which it is prepared, a small quantity being frequently sufficient. It is sometimes advisable to add other organic or inorganic materials as carriers or binding material, or for the purpose of increasing the porosity of the mass; in such cases, the introduction of substances which, like chlorine, sulphur, phosphorus, and arsenic, can act as poisons, is best avoided. If reduction to the metallic state is necessary, it should be effected at as low a temperature as possible by pure hydrogen or other suitable agent. The catalytic activity of nickel, cobalt, and iron is particularly increased. The preparation of catalysts for the conversion of carbon dioxide into methane, the hydrogenation of oils, and the reduction of nitrobenzene is described.

The second patent describes the use of other, difficultly reducible oxides of high melting point, particularly those of titanium, uranium, manganese, vanadium, columbium, or tantalum, in place of the oxides previously cited. Examples are given of the hydrogenation of cotton-seed oil and the hardening of earth-nut oil at  $100$ – $120^{\circ}$ .

H. W.

**Negative Catalysts in the Hydrogenation of Oils.**

SEIICHI UENO (*J. Chem. Ind., Tokyo*, 1918, **21**, 898—939).—The degree of the hydrogenation of oils may be indicated by the formula  $r = x/a$ , where  $r$  represents the "ratio number of hydrogenation,"  $x$  the difference between the iodine values before and after hydrogenation, and  $a$  the original iodine value of the oil. A comparison between the values of  $r$  and  $r'$  (the ratio number of hydrogenation in the absence of the particular substance) will show whether or no any given substance acts as a negative catalyst. By this means, various typical substances have been classified in accordance with their action on the catalytic hydrogenation of oils in presence of a nickel catalyst. Certain metallic soaps, such as those of potassium, barium, zinc, cadmium, lead, uranium, and gold, are injurious, whilst others, including those of calcium, aluminium, cerium, nickel, thorium, and platinum have no effect. Nickel salts of simple monocarboxylic acids, nickel lactate, and nickel salts of dicarboxylic acids (oxalic and succinic acids) have also no influence on the results. Copper hydroxide acts as a negative catalyst, but nickel hydroxide does not. Ammonium molybdate, boric acid, hydrochloric acid, and potassium hydroxide are pronounced poisons. Fatty acids, such as acetic, stearic, and oleic acids, have no effect, but hydroxystearic acids act as poisons, as do also hydroxy-acids, such as malic, citric, and tartaric acids. Certain powdered metals, such as tin, zirconium, and aluminium, have no marked action, but others, such as iron, lead, and zinc, are slightly poisonous. Other negative catalysts include sulphur, selenium, and tellurium, red phosphorus, glycerol, lecithin, alkaloids such as morphine and strychnine, potassium cyanide, and amygdalin. [See also *J. Soc. Chem. Ind.*, 1919, 20A.] C. A. M.

**Catalytic Scission of Carbon Dioxide from Keto-carboxylic Acids.**

G. BREDIG and R. A. JOYNER (*Zeitsch. Elektrochem.*, 1918, **24**, 285—298).—The rate of decomposition of camphorcarboxylic acid into carbon dioxide and camphor by the bases quinoline, 2-methylquinoline,  $\alpha$ -picoline,  $s$ -collidine, piperidine, pyridine, dimethylaniline, tribenzylamine, benzyldiethylamine, benzylamine, allylamine, triisobutylamine, diisobutylamine, isocamylamine, tripropylamine, and diethylamine has been determined in the solvents acetophenone, *o*-nitrotoluene, and *m*-xylene. The reactions were carried out at 80-2°, and the rate was determined by weighing the carbon dioxide evolved. A series of determinations made to ascertain the equilibrium between acid and the various bases in *m*-xylene solution is described. These were carried out at 20-1°. A series of molecular weight determinations of the piperidine salts of a number of acids in benzene and ethyl alcohol solutions is also described. It is shown that the rate of decomposition of camphorcarboxylic acid in xylene, acetophenone, and *o*-nitrotoluene is practically the same in all cases, but in alcohol and water the decomposition is much slower. There is no direct connexion between the affinity constants of the



bases in water and the velocity of decomposition in the above-named solvents. The action of bases on the optical rotation of camphorcarboxylic acid was investigated, and it is shown that in *m*-xylene solution the simple Oudemann law does not hold, but in some cases the extent to which the salt is split up into acid and base can be determined. In *m*-xylene solution, the bases form acid complexes with an excess of the acid, in which more than one molecule of acid is combined with one molecule of base. In the extreme case, three molecules of acid are combined with one molecule of base. The velocity of decomposition of the salts is shown in the case of a series of bases to be parallel with the number of molecules of acid which combine with one molecule of base. It is probable that every carboxylic acid forms acid complexes with bases, but picric acid does not do so. Association of the acids only occurs in those solvents in which acid complexes with bases are formed, and the catalytic decomposition of camphorcarboxylic acid only occurs in those solvents in which acid complex formation takes place between the acid and base.

J. F. S.

**The Hydrolysis of Soap Solutions, Measured by the Rate of Catalysis of Nitrosotriacetoneamine.** JAMES WILLIAM McBAIN and THOMAS ROBERT BOLAM (*T.*, 1918, 113, 825—832).

**Mercury as a Contact Poison.** G. BREDIG (*Ber.*, 1918, 51, 1477).—The poisoning of catalysts by mercury (compare Paal and Hartmann, *A.*, 1918, ii, 303) has been previously noticed by Bredig and Berneck (*A.*, 1900, ii, 213) and others.

C. S.

**Whole Number Atomic Weights and Related Questions.** R. VON MISES (*Physikal. Zeitsch.*, 1918, 19, 490—500).—A mathematical paper in which the probability that the atomic weights are whole numbers is treated.

J. F. S.

**The Atom Model of Bohr.** ARTHUR SZARVASSI (*Physikal. Zeitsch.*, 1918, 19, 504—508).—A mathematical paper in which an attempt is made to explain certain insufficiently defined points in the theory of the structure of the atom as put forward by Bohr.

J. F. S.

**Atomic Structure.** P. DEBYE and P. SCHERRER (*Physikal. Zeitsch.*, 1918, 19, 474—483).—A theoretical paper in which the rôle of the electron rings in the structure of crystals is discussed. It is shown that the electron rings of the carbon atom do not act as bonds in the structure of the diamond. The number of electrons accompanying the atoms in compounds is discussed, and some calculations are carried out in this connexion. The dimensions of the electron rings of the atoms are considered, and a method is worked out for calculating this quantity. Thus for the diamond it is shown that the radius of the electron ring is  $0.43 \times 10^{-8}$  cm., a figure which is in keeping with the value calculated by Bohr for

a ring in which four electrons are travelling round a nucleus containing four charges. In this case, the value is  $0.17 \times 10^{-8}$  cm.

J. F. S.

**Theory of Röntgen Spectra.** FRITZ REICHE and ADOLF SMEKAL (*Ann. Physik.*, 1918, [iv], 57, 124—144).—A theoretical paper in which the relative positions of the *K* and *L* electron rings are discussed. Assuming the hypothesis of Debye and Vegard, and neglecting the electric and magnetic disturbances between the *K* and *L* rings, the formula  $\Delta = v_{La}/R - 5/36z^2 = B_{p_1p_2} \cdot z + C_{p_1p_2}$  is deduced. In this equation,  $v_{La}$  is the vibration number of the *L<sub>a</sub>* line, *R* the Rydberg number, *z* the atomic number of the element,  $B_{p_1p_2}$  and  $C_{p_1p_2}$  are functions of  $p_1$  and  $p_2$ , the number of electrons in the *K* and *L* rings respectively. The values of  $v_{La}/R$  and  $5/36z^2$  are evaluated for the elements of atomic numbers 30–92, and it is shown that up to 58 the agreement is linear, and above this number the divergence is very small, so that it becomes necessary to take the disturbances into account in such calculations.

J. F. S.

**Coupling of Electron Rings and Optical Activity of Asymmetric Molecules.** A. LANDÉ (*Physikal. Zeitsch.*, 1918, 19, 500—504).—A mathematical paper in which the connexion between the optical activity of asymmetric molecules and the electron rings is treated.

J. F. S.

**Systematic Valency Theory and the Explanation of this Theory of Complex Compounds. Ionogen and Labile Bonds, Gaseous Molecules, Polymerisation and Isomerisation.** EMIL KOHLWEILER (*Zeitsch. physikal. Chem.*, 1918, 93, 113—153).—A continuation of the work previously published (*A.*, 1918, ii, 304).—It is shown in the present paper that the views put forward to explain the formation and stability of compounds of the first order are equally applicable to compounds of higher orders. Particularly it is shown that the mechanism of the formation of molecular and complex compounds is the same as that of simple compounds in respect of the method of linking. The origin of ionogen and non-ionogen bands, polymerisation and isomerisation, the constitution of explosives and unstable compounds, and that of the gaseous molecules, are explained on the basis of this theory. For details of these points the original paper should be consulted.

J. F. S.

**Apparatus for Facilitating the Manipulation of Gases.** MAX BODENSTEIN (*Ber.*, 1918, 51, 1640—1645).—(1) A vacuum tube opener similar to that described by Stock (*A.*, 1918, ii, 353) has been used by the author for more than twenty years. (2) A stopcock is described the extremities of the stopper of which are surrounded by the gas under manipulation, so that the intrusion of air is impossible. (3) A mercury gasometer is described which

requires the use of very little mercury. (4) A fatless metallic stopcock and (5) a quartz Bourdon manometer are also described. The first three pieces of apparatus are figured. C. S.

**Condenser.** R. HOWDEN (*Chem. News*, 1918, 117, 368).—The apparatus consists of a test-tube 2.5 cm. in diameter and 20 cm. long, which is placed in a vessel through which cold water is circulated. The tube is closed by a cork through which pass the tube from the distillation flask, and a second tube which extends from the bottom of the test-tube, the upper end of this second tube being bent downwards into a receiver. The first portion of the distillate collects in the test-tube; as further quantities collect, the contents of the test-tube are forced over into the receiver. W. P. S.

**Two Lecture Experiments.** FR. FICHTER (*Helv. Chim. Acta*, 1918, 1, 430—432).—(1) *Absorption of Gases by Water.*—In demonstrating the absorption of very soluble gases by water, it is usual to collect them over mercury and then to admit water; in order to obtain the gas free from air and to collect over mercury without allowing it to escape into the atmosphere, the author recommends the use of a eudiometer, the upper end of which is drawn out into a tube connected through a stopcock with a T-piece. The eudiometer is filled with mercury up to the stopcock. The gas is then passed through the open limb of the T-piece until a test sample dissolves completely in water; it is then passed into the eudiometer by cautiously opening the cock. The experiment is completed as usual. (2) *Preparation of Calcium Carbide without an Electric Furnace.*—A quantity of compressed carbon dioxide snow is placed on an iron dish and covered with finely divided calcium mixed with loose solid carbon dioxide; reaction is started by allowing burning calcium to fall on the mixture, and proceeds vigorously. The presence of calcium carbide and nitride is demonstrated in the usual manner. Formation of the latter is inhibited as far as possible by using a considerable excess of carbon dioxide. The calcium must be in a finely divided state; large pieces only react superficially, and the presence of free calcium in the product causes the acetylene evolved, on addition of water, to be so largely diluted with hydrogen that it does not give a smoky flame. H. W.

## Inorganic Chemistry.

**The Determination of the Molecular Complexity of Liquid Sulphur.** ALEX. MITCHELL KELLAS (T., 1918, 113, 903—922).

**Occurrence of Hydrogen Selenide in Rain and Snow.** P. KARRER (*Helv. Chim. Acta*, 1918, 1, 499).—Repetition of Gassmann's experiments (A., 1918, ii, 309) has led the author to the conclusion that selenium is not present in snow or rain. H. W.

**Starting and Stability Phenomena of the Oxidation of Ammonia and Similar Reactions.** F. G. LILJENROTH (*Chem. and Met. Eng.*, 1918, 19, 287—293).—Conversion curves have been plotted for the oxidation of ammonia at various temperatures, showing that whilst little oxidation takes place at 400°C, it rises rapidly between 450° and 500° to nearly 100%, reaches a maximum at about 750°, and then decreases first slowly and afterwards rapidly. The temperature of the gauze or catalyst may also be plotted for various percentages of ammonia-oxidation, and the curve is found to be a straight line, the position of the line, termed the "heat of reaction line," on the conversion curve diagram depending on (1) the initial temperature of the gas, and (2) the initial composition of the gas. The effects of changes in the velocity and the composition of the gaseous mixture on the relative positions of these two curves are described, and the conditions for (1) the cessation of the reaction, (2) overcoming the prejudicial effects of catalytic poisons, are indicated. The reaction does not start spontaneously, but must be initiated by heating to a particular ignition temperature, which is below the reaction temperature. The use of oxygen is shown to be not justified, as it merely results in a higher temperature, necessitating water cooling of the gauze. A cheap low-grade catalyst may be possible for the first gauze, and a platinum gauze for completion of the oxidation in a manner analogous to the sulphuric acid process. The synthetic ammonia process is also considered, and it is shown that in this case a heat exchanger must always be used, and additional heat must usually be supplied. With a high pressure and a good catalyst, however, no heat need be supplied except during the starting period.

B. N.

**The Oxidation and Ignition of Coal.** RICHARD VERNON WHEELER (T., 1918, 113, 945—955).

**Oxidation of Carbon Monoxide in Contact with Copper.** K. A. HOFMANN (*Ber.*, 1918, 51, 1334—1346).—Continuing his search for a reagent to oxidise carbon monoxide at the ordinary temperature (A., 1916, ii, 637), the author has shown that hydrated

copper oxide in the presence of aqueous alkali converts carbon monoxide into a carbonate, although at only a slow rate. The addition of platinum metals, especially iridium, increases the rate five times. In contact with metallic copper moistened with aqueous alkali carbon monoxide mixed with air is oxidised two or three times more rapidly than it is when in contact with a copper oxide surface of the same area. The copper is converted into a peroxide,  $\text{Cu}_2\text{O}_3$  or  $\text{CuO}_2$ , which is the real oxidising agent. The addition of a trace of iridium to the copper does not change the oxidising power of the peroxide, but increases the adsorptive capacity of the surface for carbon monoxide, and thus increases the rate of oxidation. It is very remarkable that the rate of oxidation of hydrogen in contact with an alkaline copper surface is only 1/70 (with addition of iridium, 1/50) of that of carbon monoxide, the copper surface having a very small capacity of adsorbing molecular hydrogen. The experiments were performed in a Hempel gas pipette filled with rolls of copper gauze moistened with 15% potassium hydroxide solution. The concentration of the alkali does not appreciably affect the results.

C. S.

**The Action of Chlorine on the Alkali Iodides.** WILLIAM NORMAN RAE (T., 1918, 113, 880—884).

**Literature on the Solubility of Systems Relating to Nitre Cake.** H. W. FOOTE (*J. Ind. Eng. Chem.*, 1918, 10, 896—897).—A résumé of the literature dealing with the solubility relationships of the systems,  $\text{Na}_2\text{SO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ ;  $\text{Na}_2\text{SO}_4\text{--RSO}_4\text{--H}_2\text{O}$ ; and  $\text{RSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$  ( $\text{R}=\text{Fe}^{\text{II}}$ , Cu, Ba, Ca,  $\text{Gf}$ , etc.).

J. F. S.

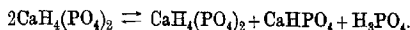
**Recrystallisation of Nitre Cake.** BLAIR SAXTON (*J. Ind. Eng. Chem.*, 1918, 10, 897—901).—Equations, based on solubility determinations, have been developed, by means of which the amount of any one solid phase, that can be separated from the system  $\text{Na}_2\text{SO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ , can be calculated if the composition of the original nitre cake and the acid concentration after crystallisation are known. These equations are for the temperature  $25^\circ$ . Further equations are given for the same temperature, by means of which the amount of water to be added to the nitre cake may be calculated in order to leave a calculated amount of one of the solid phases. Further equations for obtaining the maximum amount of each solid phase from solution at temperatures of  $0^\circ$  and  $25^\circ$  are also given. Leaching processes are outlined, by means of which sulphuric acid may be concentrated in the solution and sodium sulphate in the solid. It is found experimentally that this separation can be carried out more efficiently at  $0^\circ$  than at  $25^\circ$ . J. F. S.

**Colloidal Silver.** ALWYN PICKLES (*Chem. News*, 1918, 117, 358).—When well-washed silver oxide is reduced by a rapidly stirred 60% solution of formaldehyde, a solution of colloidal silver is produced. This solution is very stable, and varies in colour from pale

black to rich ruby-red. Acetaldehyde has not the same effect, and with formaldehyde the coloured solutions are only produced at about 35°. The colour is discharged slowly by salt solutions, and by nitric acid. Hydrogen peroxide is slowly decomposed by the solution.

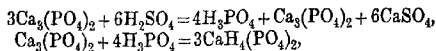
J. F. S.

**Rational Preparation of Superphosphates.** A. AITA (*Annali Chim. Appl.*, 1918, 10, 45—103).—On dissolving increasing quantities of monocalcium phosphate in a given weight of water at constant temperature the proportion of free phosphoric acid continually increases, and tends towards a limit in accordance with the equation

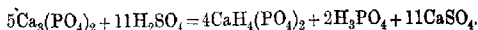


Up to the saturation point at 15° there would thus be a liquid phase consisting of water, monocalcium phosphate, and free phosphoric acid, and a solid phase consisting solely of dicalcium phosphate formed by hydrolysis of the monocalcium phosphate. Beyond the saturation point, with increasing quantities of calcium oxide and phosphoric oxide, the liquid phase remains unaltered, whilst the solid phase is constantly enriched by monocalcium phosphate. On raising the temperature the decomposition of the monocalcium phosphate is accentuated, whilst the saturation point is retarded. Monocalcium phosphate appears in the solid phase at the same limit of concentration for the calcium oxide, but at a greater concentration of the phosphoric oxide. In the case of commercial superphosphates containing about 12—20% of soluble phosphoric oxide and 10—20% of water, there is a system with a fairly high proportion of phosphoric oxide, and a very low proportion of water. In estimating free phosphoric acid in such products it is necessary to use anhydrous ether for the extraction, since water, alcohol, or ordinary ether cause more or less hydrolysis of the monocalcium phosphate, according to the amount of water originally present. The physico-mechanical properties of superphosphates depend on the proportion of free phosphoric acid and water, the former depending on the nature and physical conditions of the components of the reaction, and the latter mainly on the concentration of the sulphuric acid used in the preparation. On these grounds commercial superphosphates may be classified as *normal* or *abnormal* products, the former containing not more than 10—12% of water or 1—2% of phosphoric oxide as free phosphoric acid (about 5—10% of the total soluble phosphoric oxide). Dicalcium phosphate is invariably present, and the fraction of phosphoric oxide in that form of combination should be equal to that present as free phosphoric acid. The mono- and dicalcium phosphates and calcium sulphate are mainly present in the hydrated form. In the case of superphosphates of abnormal constitution the water of the liquid phase exceeds 12%, and the free phosphoric acid exceeds 2% or 10% of the soluble phosphoric oxide, whilst the salts are mainly in the crystalline condition, and there is little or no dicalcium phosphate present. It is commonly

accepted, in accordance with Kolb's view, that the reaction between sulphuric acid and mineral phosphates takes place in two stages:



but the observed facts show that the main reaction is more correctly represented by the equation:



The influence of raising the temperature on the reaction is to increase the concentration of free phosphoric acid in the liquid phase, whilst in the solid phase the dicalcium phosphate increases in equal proportion with the free phosphoric acid. These constituents gradually interact to form monocalcium phosphate, so that the existence of dicalcium phosphate in an industrial product will depend on the proportion of free phosphoric acid originally present. Hence in products prepared with an excessive quantity of sulphuric acid, and thus containing a high proportion of free phosphoric acid, the dicalcium phosphate will be reduced or disappear altogether. In fact, monocalcium phosphate is not hydrolysed in presence of an excess of phosphoric acid, and in such cases the solid phase of the system will consist solely of monocalcium phosphate. The application of these principles to the industrial preparation of superphosphates yields products with the desired physico-mechanical properties. [See also *J. Soc. Chem. Ind.*, 1919, 23A.] C. A. M.

**The Decomposition of Barium Peroxide and the Re-activity of the Resulting Barium Oxide.** J. ARVID HEDVALL (*Zeitsch. anorg. Chem.*, 1918, 104, 163—168).—The decomposition of barium peroxide by heat at atmospheric pressure has been followed by means of the heating curve. The peroxide was heated in a carbon tube furnace and the temperature recorded at 10 sec. intervals by means of a platinum—platinum—rhodium thermoelement. The reaction being endothermic, its range is indicated on the heating curve by a pronounced flattening towards the time axis. The temperature at which the vapour pressure of the evolved oxygen is equal to 760 mm. was found to be 795°. This agrees with the value 796° found by Le Chatelier. The higher temperature, 825°, obtained by Hildebrand is accounted for by the fact that this observer used very carefully dried materials, for in the absence of moisture the reaction is very slow and incomplete.

In presence of copper oxide, barium peroxide starts to decompose at about 200°, the reaction becoming most vigorous at 625—660°. as shown by the heating curve. When the peroxide is heated with amorphous silica, however, the rate of rise of temperature increases above 400°. The endothermic decomposition of the peroxide is evidently accompanied by a more strongly exothermic reaction, probably the formation of a barium silicate, brought about by the great reactivity of the barium oxide at the moment of its formation. Even when powdered quartz glass or crushed quartz is used

in place of amorphous silica, there is evidence in the heating curve of silicate formation.

E. H. R.

**Solubility of Cupric Hydroxide, to a Certain Concentration in Sodium Hydroxide and Potassium Hydroxide.** ED. JUSTIN-MUELLER (*Compt. rend.*, 1918, 167, 779—780).—Cupric hydroxide dissolves in aqueous sodium hydroxide (D 1.345—1.370) or aqueous potassium hydroxide (D 1.453—1.498) to the extent of 0.78 gram in 100 c.c., giving bright blue solutions which do not give any precipitate when boiled directly or first diluted and then boiled. Solutions prepared with more dilute alkali are not stable.

W. G.

**Scandium from a Brazilian Source.** C. JAMES (*J. Amer. Chem. Soc.*, 1918, 40, 1674).—Whilst working up quantities of Brazilian zirconia the author obtained a gelatinous residue which on examination was shown to consist of scandium fluoride.

J. F. S.

**Rare Earths. VIII. Separation of Yttrium from Erbium; The Ratio  $\text{Er}_2\text{O}_3:2\text{ErCl}_3$ .** EDWARD WICHES, B. S. HOPKINS, and C. W. BALKE (*J. Amer. Chem. Soc.*, 1918, 40, 1615—1619. Compare A., 1917, ii, 34).—Using material containing only erbium and yttrium, the authors have investigated the newer methods proposed for the separation of these two elements. The cobalticyanide and the nitrite precipitation methods were found to give good results, the latter being the more efficient and practicable. The older nitrate fusion method was found to give results far superior to the other methods, and by this method erbium compounds of a high degree of purity were obtained. The ratio of erbium oxide to erbium chloride was determined in seven analyses. The ratio was found to vary with the temperature and length of time of ignition of the oxide. Erbium oxide, prepared by the ignition of the oxalate and ignited for several hours at  $800^\circ$  and two hours at  $900^\circ$ , was found to retain considerable amounts of carbon dioxide. This is contrary to Hofmann's results (A., 1910, ii, 1073), and consequently brings into disrepute the present accepted value of the atomic weight of erbium. Until erbium oxide of the definite composition  $\text{Er}_2\text{O}_3$  is prepared, no ratio in which the oxide is one term can be trustworthy for the purpose of atomic weight determinations.

J. F. S.

**Preparation and Properties of Yttrium Mixed Metal.** J. F. G. HICKS (*J. Amer. Chem. Soc.*, 1918, 40, 1619—1626).—Experiments of a preliminary nature dealing with the preparation of yttrium mixed metal are described. It is shown that the method of preparing anhydrous chlorides of the metals of the yttrium earths, by heating the hydrated chlorides with ammonium chloride to drive off five of the six molecules of water of crystallisation, and then in a current of hydrogen chloride to remove the



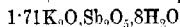
last molecule of water, is capable of being used on the large scale. The mixed metal has been prepared in the form of powder by heating the anhydrous chlorides with sodium in a vacuum at  $1100^{\circ}$ , and also by electrolysis of a mixture of the molten chlorides in a protected graphite crucible, using a graphite anode. Electrolysis of a solution of the mixed oxides in fused cryolite also yields the mixed metal in the form of powder, but the method is less efficient than the foregoing methods. In all these processes, there is considerable loss of yttrium chloride, owing to its volatility at the temperature of the experiments. The powdered products have been obtained in a coherent form by sintering in a vacuum, but the resulting mass easily disintegrates. The product obtained has a mean "atomic weight" of 120 and contains 94.05–95.70% of metal, which corresponds with 37.5% of yttrium. It burns in the air at a dull red heat with a very bright light, and yields a light brown oxide. It is slowly oxidised by moist air at the ordinary temperature. It glows when heated in hydrogen, nitrogen, or carbon dioxide. It does not amalgamate with mercury, and is readily attacked by water. Yttrium mixed metal is pyrophoric, but not so strongly as the cerium metal iron alloys. J. F. S.

**Effects of Heat on Chemical Glassware.** R. G. SHERWOOD (*J. Amer. Chem. Soc.*, 1918, **40**, 1645–1653).—When glass is heated, there is shown to be evidence of two distinct kinds of gaseous evolution, that resulting from adsorbed material, which is readily removed at temperatures below  $300^{\circ}$ , and that resulting, in all probability, from a decomposition of the glass itself. The latter effect becomes important above  $400^{\circ}$  for the softer glasses and above  $500^{\circ}$  for the harder glasses. There is some evidence of a definite characteristic rate of gaseous evolution for each temperature to which glass is subjected, increasing with the temperature and extending over a considerable period. Observations on one sample at  $500^{\circ}$  showed a small, continuous evolution even after heating for twenty hours. Adsorption products are confined to quantities which are represented approximately by a layer of gas about one molecule deep, and are removed with much greater rapidity at lower temperatures than the other products obtained, which are due to the heating of the glass. The most important of the gaseous evolution products obtained from glass under the influence of heat is water, which, as the temperature is raised to the softening point of the glass, constitutes almost the entire quantity of the evolution, but its amount at a lower temperature may be relatively unimportant. J. F. S.

**Plasticity and 'Strength' of Clay.** OTTO NOLTE (*Bied. Zentr.*, 1918, **47**, 108–109).—Extraction of a heavy Silesian clay with alcohol and ether did not cause any diminution in the plasticity or 'strength' of the clay. The presence of a certain proportion of organic matter, therefore, does not affect these qualities of the clay. The extract was found to contain sulphur and an organic compound which was not identified. H. W. B.

**Zirconyl Basic Chromate.** F. P. VENABLE and L. V. GILES (*J. Amer. Chem. Soc.*, 1918, **40**, 1653—1656).—A basic zirconium chromate is prepared as a granular, yellow precipitate by dissolving zirconium hydroxide in a boiling solution of chromic acid, diluting, and again boiling the solution. The compound obtained loses a considerable quantity of its water at 110°, but the whole of it is only lost at 200°. The compound is shown to have the formula  $2\text{ZrO}(\text{OH})_2 \cdot \text{ZrO} \cdot \text{CrO}_4 \cdot 8\text{H}_2\text{O}$ , and it is suggested that its formation occurs as follows: first, normal zirconium chromate is formed, which is immediately hydrolysed to  $\text{ZrO} \cdot \text{CrO}_4$ ; some of the zirconium hydroxide is partly dehydrated to give  $\text{ZrO}(\text{OH})_2$ . These two substances then combine to give the yellow, insoluble compound described above. The present work is at variance with earlier work on zirconium basic chromates by Haber (*A.*, 1897, ii, 295). J. F. S.

**Antimonic Acids and Antimonates.** GERHARDT JANDER (*Kolloid Zeitsch.*, 1918, **23**, 122—144).—Analyses of the various hydrates of antimony pentoxide have been made, and the dehydration curves of these compounds obtained by keeping them over sulphuric acid in a desiccator. The behaviour of the antimonic acids toward hydrochloric and sulphuric acids and toward solutions of potassium and sodium hydroxides has been studied. The potassium and sodium salts of these acids have also been investigated. The experiments show that the properties of the antimonic acids vary with the method of preparation and with previous treatment. Thus, modifications which differ in their water content, stability, solubility, and their behaviour towards acids and alkalis are obtained (i) by the action of water on the pentachloride, (ii) by the action of acids on antimonates, and (iii) by the hydrolysis of the trichloride in the presence of nitric acid. These varieties of antimonic acid differ only slightly from one another, and probably, as in the case of the stannic acids, the difference is due to a difference in the size of the particles. The experiments indicate that the tri- and tetra-antimonic acids, that is, the soluble antimonic acids, are hydrosols of small stability, and that the definite hydrates of antimony pentoxide known as ortho-, pyro-, and meta-antimonic acid can have no free existence. The hydrates of antimony pentoxide exhibit a marked selective absorption towards dilute alkalis. Thereby are formed amorphous substances, which apparently are alkali antimonates. The composition of these substances, however, varies continuously with the composition of the solid hydrate. In concentrated alkali solutions, the hydrates of antimony pentoxide dissolve, and from these solutions at low temperature and by careful evaporation, various alkali antimonates may be crystallised, but the nature of the salt depends on the concentration of the mother liquor. The compound



has been obtained in this way.

J. F. S.

**Bismuth Hydride.** FRITZ PANETH (*Zeitsch. Elektrochem.*, 1918, 24, 298—299).—Working from the point of view that isotopes and their compounds are identical, the author is of the opinion that bismuth hydride is capable of existence, and that it is gaseous and only moderately stable, much less so than antimony hydride. These statements are based on the fact that by the action of hydrochloric acid on magnesium which has been covered with thorium-C (an isotope of bismuth), a radioactive hydride is produced which has the properties enumerated above. J. F. S.

**Hydroxylamine Platinum Bases.** LEO ALEXANDROWITSCH TSCHUGAEV and ILJA ILJITSCH TSCHERNJAEV (*T.*, 1918, 113, 884—897).

### Mineralogical Chemistry.

**"Hydromagnocalcite" from the Tatra Mountains, Carpathians.** EMANUEL GLATZEL (*Centr. Min.*, 1918, 307—311).—The compact, chalk-white material with conchoidal fracture is found as loose blocks in the Lopusna valley, near the village of Lucsivna, on the southern slopes of the Tatra Mountains. Analysis gave results approximating to the formula  $\text{CaCO}_3 + \text{Mg}(\text{OH})_2$ .

CaO.	MgO.	CO <sub>2</sub> .	H <sub>2</sub> O.	Total.	Sp. gr.
36.55	23.15	28.75	10.60	99.05	2.412

[This is evidently penecatite, which was long ago proved to be a mechanical mixture of calcite and brucite ( $\text{Mg}(\text{OH})_2$ ).]

L. J. S.

### Analytical Chemistry.

**Quantitative Analysis of Small Quantities of Gases.** H. M. RYDER (*J. Amer. Chem. Soc.*, 1918, 40, 1656—1662).—A somewhat complicated apparatus is described by means of which a quantitative analysis of 5 cu. mm.—1 c.c. of a gaseous mixture of water vapour, carbon dioxide, carbon monoxide, oxygen, hydrogen, nitrogen, and methane may be carried out with an accuracy of about 5% for each constituent. The apparatus makes use of a McLeod gauge and an optical lever gauge, but for details the original should be consulted. J. F. S.

**Gas Bubbler for Gas Analysis.** OLIVER D. BURKE (*Chem. News*, 1918, 117, 368—369).—The glass tube through which the

gas enters is drawn out into a fine capillary. Another glass tube is fused on to the side of the first tube and bent so that the end extends just below the end of the capillary, where it is flattened and the top surface ground. The capillary is made to fit tightly on the ground surface, so that the gas escaping from the capillary is broken up into very fine bubbles. [See, further, *J. Soc. Chem. Ind.*, January, 1919.] W. P. S.

**Oxidising Action of Potassium Dichromate as Compared with that of Pure Iodine.** CARL R. MCCROSKY (*J. Amer. Chem. Soc.*, 1918, **40**, 1662—1674).—The author has studied the trustworthiness of potassium dichromate as a standardising agent in iodometric determinations. It is shown that potassium dichromate always liberates more than the theoretical quantity of iodine from hydriodic acid. This excess of iodine may be reduced, but not wholly removed, by removing dissolved air from the solutions, by drying, and fusing the dichromate in the absence of air and by recrystallising repeatedly to remove oxidising impurities. It is also shown that the excess of iodine is not due in any way to the catalytic action of chromium chloride. J. F. S.

**Estimation of Active Oxygen in Sodium Peroxide.** JAROSLAV MILBAUER (*J. pr. Chem.*, 1918, [ii], **98**, 1—8).—The following methods have been proposed for the estimation of active oxygen in sodium peroxide: (1) liberation of hydrogen peroxide by water followed by titration with potassium permanganate, (2) treatment of sodium peroxide with potassium iodide and potassium hydrogen carbonate, and titration of the iodine liberated with sodium arsenite, and (3) measurement of the oxygen liberated by water in the presence of cobalt nitrate. The results obtained by the first method are very low, those by the second are somewhat better, but still low, whilst the third method gives high results. The methods have been critically examined and improved; the following processes yield accurate results: (1) Water (100 c.c.) is mixed with concentrated sulphuric acid (5 c.c.) and chemically pure boric acid (5 grams); sodium peroxide (0.5 gram) is gradually added to the mixture, which is kept briskly shaken, and the liberated hydrogen peroxide is titrated with potassium permanganate. The usual permanganate method gives low results, since a portion of the hydrogen peroxide is catalytically decomposed by the manganese sulphate formed during the process. (2) Sodium peroxide is gradually introduced into a solution of potassium iodide (2 grams) in dilute sulphuric acid (1 in 20; 200 c.c.); the iodine is titrated with standard thiosulphate. The results agree fully with those obtained by the permanganate method. (3) Sodium peroxide (0.2—0.3 gram) is mixed with about 10 c.c. of copper sulphate solution (0.05%) in a small flask connected to a nitrometer; the flask is shaken, and decomposition is complete within a minute, when the liberated oxygen is measured. The gas evolved contains about 0.32% of carbon dioxide and 0.08% of

hydrogen. With cobalt nitrate as catalyst, the results are invariably high; the authors consider this may indicate the presence of an oxide higher than the peroxide.

The action of the atmosphere on sodium peroxide has also been investigated; moisture appears to be more active than carbon dioxide in causing decomposition. H. W.

**Pregl's Micro-estimation of Nitrogen.** HANS FISCHER (*Ber.*, 1918, 51, 1322—1325).—The estimation of nitrogen in difficultly combustible substances by the micro-Dumas method (compare Dubsy, A., 1918, ii, 130) gives untrustworthy results, and the author now employs only the original Pregl method. The causes of the inaccuracies in the former method are discussed.

The author uses the micro-Pregl method in preference to the Lassaigue test for the detection of nitrogen in rare or very valuable organic compounds. C. S.

**Detection and Estimation of Hydrogen Phosphide in Hydrogen.** J. SOYER (*Ann. Chim. anal.*, 1918, 23, 221—225).

—Hydrogen prepared by the action of sodium hydroxide on ferro-silicon always contains traces of hydrogen phosphide. The presence of the latter may be detected by burning the hydrogen from a platinum jet and directing the flame on to the edge of a porcelain basin; the flame has a green coloration. When examined with the spectroscope, the flame exhibits the phosphorus spectrum. If a drop of water suspended on a glass rod is held in the flame for fifteen seconds and then tested with molybdic acid reagent, a yellow precipitate is obtained. The amount of hydrogen phosphide present is estimated by passing a definite volume (from 2 to 20 litres) of the gas, together with a large excess of air, through a platinum jet arranged in a silicon tube heated to bright redness; this tube is inclined slightly, and its lower end is connected with absorption vessels containing water. When the desired quantity of the gas has been burned, the tube and the contents of the absorption vessels are rinsed into a basin, treated with 5 grams of ammonium nitrate, concentrated to about 40 c.c., and the phosphoric acid precipitated with molybdic acid reagent. [See, further, *J. Soc. Chem. Ind.*, 1918, 765A.] W. P. S.

**Estimation of Minute Quantities of Arsenic.** O. BILLETER (*Helv. Chim. Acta*, 1918, 1, 475—498).—A more extended and somewhat modified account of the method previously published (*A.*, 1915, ii, 578).

The estimation of arsenic in organic substances is effected in the following manner. The organic matter is destroyed either by treatment with a mixture of nitric and concentrated sulphuric acids or, in the case of urines, by rendering the latter alkaline with sodium carbonate, evaporation to a syrup, admixture with potassium perchlorate (2 grams) and potassium sulphate (4 grams) for each 100 c.c. of urine, desiccation of the mixture at 120°, and

gradual introduction of the latter into a platinum crucible heated to dull redness, followed by more intense ignition until tranquil fusion is attained. The arsenic is separated from other metals by distillation with a mixture of sodium chloride (2 grams) and potassium bromide (0.2 gram) for each 20 c.c. of sulphuric acid (the addition of hydrazine sulphate previously recommended is found to be unnecessary), or, if destruction of organic matter has been effected with potassium perchlorate, by treatment with potassium bromide (0.1—0.2 gram) and sulphuric acid (90%, 6 c.c.). Mercury is completely retained by one distillation, but if antimony is present, it is necessary to redistil after addition of 5—6 grams of sulphuric acid (90%). Hydrochloric acid is eliminated from the distillate by treatment with hypochlorous acid, and the solution is evaporated to dryness. The residue is dissolved in sulphuric acid (12%, 1 c.c.) and evaporated on the water-bath to destroy any chloric acid that may be present; after addition of water (0.85 c.c.), it is transferred to a Marsh's apparatus. By this method, 0.01 mg. of arsenic may be detected.

The precautions necessary for ensuring the requisite purity of the reagents are fully described. The commercial pure sulphuric acid is diluted to 85% and heated with sodium chloride (3%) and potassium bromide (0.3%) in a quartz flask; the treatment is twice repeated with smaller quantities of salts, and the acid is finally distilled from a quartz retort and collected in a quartz flask. The nitric acid and the salts are purified by Lockemann's method. Zinc is conveniently obtained by the electrolysis of an aqueous solution of zinc sulphate, using a zinc anode and copper cathode; the metal is obtained in the pulverulent state, and dissolves readily in dilute sulphuric acid without being activated. It is free from arsenic. Hypochlorous acid is best prepared by the solution of chlorine monoxide in water.

The sensitiveness and constancy of the arsenic mirrors depend considerably on the quality of the calcium chloride used in desiccating the gas. Commercial fused calcium chloride is unsuitable, as it is always strongly alkaline; a neutral product can be obtained by dehydrating the crystalline substance at 200°, and subsequently gradually heating the finely divided product to its melting point in a quartz tube in a slow current of dry hydrogen chloride. The best results are obtained by starting from metallic calcium.

H. W.

**Amount of Amorphous Silica in the Soil.** BÉLA VON HORVÁTH (*Bied. Zentr.*, 1918, 47, 97—98).—For the estimation of the amorphous silica, 5 grams of the soil are extracted with 100 c.c. of a 1% sodium carbonate solution for fifteen minutes at 100°. Solutions of sodium carbonate of greater concentration than 1% dissolve silicates and quartz besides amorphous silica, the results obtained being consequently too high. When estimated by the author's method, soil is found to contain only a few milligrams per cent. of amorphous silica.

H. W. B.

**Estimation of Metals by Electrolytic Deposition without using an External Supply of Electricity.** MAURICE FRANÇOIS (*Compt. rend.*, 1918, 167, 725—727).—A strip of nickel is placed across the top of a platinum crucible, and a zinc rod, 5 mm. in diameter, is suspended from the strip; the rod is notched so as to fit on to the nickel strip, and the lower end of the rod extends nearly to the bottom of the crucible. The zinc rod is amalgamated at least twenty-four hours before being used, and is wrapped in filter-paper, which is tied on to the rod with ordinary cotton thread. The electrolyte used for the deposition of silver or gold consists of 9 c.c. of 10% potassium cyanide solution, 5 c.c. of potassium hydroxide solution (D 1.332), and 2 c.c. of ammonia; for the deposition of mercury, the solution should consist of 20 c.c. of 10% sulphuric acid containing 0.5 gram of potassium iodide. In all cases, the deposition requires twenty-four hours for completion. [See, further, *J. Soc. Chem. Ind.*, 1918, 784A.]

W. P. S.

**Quantitative Estimation of Ions by Microanalytical Methods. I.** ROBERT STREIBINGER (*Österr. Chem. Zeit.*, [ii], 21, 71—73; from *Chem. Zentr.*, 1918, ii, 471).—The author has extended Pregl's method of quantitative organic microanalysis to inorganic substances, and describes the estimation of silver, nickel, arsenic, iron, chromium, and copper, and the separations of silver from copper and lead from tin. Precipitation of nickel with  $\alpha$ -benzildioxime is unsuitable for microanalytical purposes, the results being too high.

H. W.

**Gravimetric Analysis. VI. Estimation of Calcium. VII. Separation of Calcium from Magnesium.** L. W. WINKLER (*Zeitsch. angew. Chem.*, 1918, 31, 187—188, 203, 214—216).—Estimation of calcium as oxalate or carbonate was submitted to critical examination. It is recommended that the precipitation as oxalate should be made from an acetic acid solution in the presence of ammonium chloride; the calcium oxalate should be weighed as such, since ignition to oxide is less trustworthy, especially in the presence of sulphates. If the latter are present, the oxalate always contains sulphate, but the weight is not affected, since the two have practically identical molecular weights. For the separation of calcium from magnesium, the calcium is precipitated as described from an acetic acid solution; the magnesium is subsequently precipitated as ammonium magnesium phosphate and weighed in this form. [See, further, *J. Soc. Chem. Ind.*, 1919, 29A.]

W. P. S.

**Estimation of Calcium and Magnesium in different Saline Solutions.** E. CANALS (*Bull. Soc. chim.*, 1918, [iv], 23, 422—430).—The simplest and most satisfactory method of estimating calcium is to precipitate it as oxalate in ammoniacal solution and weigh it as oxide. The method of precipitation as

sulphate and weighing as such is also very exact, providing that numerous precautions are taken. [See, further, *J. Soc. Chem. Ind.*, January, 1919].

W. G.

#### Sensitiveness of the most usual Tests for Copper.

A. WÖBER (*Osterr. Chem. Zeit.*, [ii], 21, 105—107; from *Chem. Zentr.*, 1918, ii, 560).—The usual tests for the detection of copper have been investigated with respect to sensitiveness with a view to their application in microanalysis; the results are given in the form of a table.

H. W.

#### Separation of Hydroxides in the Ammonium Sulphide Group.

W. D. TREADWELL (*Schweiz. Chem. Zeit.*, 1918, 2, 50—61, 71—74; from *Chem. Zentr.*, 1918, ii, 663—664).—The separation of bivalent from trivalent metals of the ammonium sulphide group by simple precipitation with dilute ammonia from solutions containing ammonium salts is generally not quantitative. Transitory local excess of the reagent cannot be avoided, and the precipitate then carries down varying amounts of the bivalent metal. The necessary asymptotic approach to the neutral point can be easily attained by leading a current of dilute ammonia (obtained by blowing air through a saturated solution of ammonium chloride in the presence of calcined magnesite) through the solution. Precipitation by the gas has the advantage that it is possible to approach the neutral point with the necessary caution without correspondingly diluting the solution. In the presence of manganese, ammonia should not be added until neutralisation is complete, since the manganese ion is readily oxidised by air in neutral solution and passes into the precipitate; neutrality to litmus is the farthest possible limit. In the separation of chromium and manganese, the latter is always adsorbed by the chromium hydroxide. The hydroxides of the trivalent metals carry down nickel and cobalt more readily than manganese and zinc. The error can be somewhat diminished by precipitating and filtering the main portion of the sesquioxides in distinctly acid solution, and subsequently precipitating the remainder from the filtrate after fresh addition of ammonium salts. The precipitates contain much more basic sulphate than chloride. Precipitates from solutions containing sulphates are more sandy in character and do not adhere to glass; when washed, they lose the sulphate ion and become slimy.

Mercuric oxide is not suitable for the precipitation of the trivalent metals of the ammonium sulphide group as hydroxides. When warmed with dilute ammonium sulphate solution, it only liberates an insufficient quantity of ammonia; addition of ammonium chloride effects an improvement, due to the formation of complex mercury salts. The precipitates are very easily filtered; they are ignited wet, when the admixed mercury compounds are quantitatively volatilised.

For the precipitation of aluminium, chromium, and iron, a



freshly prepared mixture of sodium or potassium nitrite and ammonium chloride is to be preferred to the very unstable ammonium nitrite. The precipitates obtained from solutions of ferric salts by this process are very difficult to filter, and are greatly contaminated with basic salts. The difficulty may be avoided by displacing the nitrous acid from the solution by a current of inert gas at the temperature of the water-bath. The utility of the method is limited owing to the oxidising action of the nitrous fumes.

A portion of the aluminium remains in solution when a dilute solution of aluminium chloride is precipitated by sodium thio-sulphate and boiling is continued until sulphur dioxide is completely expelled; precipitation is still less complete in the case of chromium. H. W.

**Arsenite Titrations of Permanganate Solutions.** ALONE BOSE (*Chem. News*, 1918, 117, 369—370).—Results of experiments are recorded showing that free nitric acid is not the cause of the abnormally high reducing value of sodium arsenite solution when this is used for the titration of permanganate (compare Ibbotson, A., 1918, ii, 175). The formation of manganic compounds does not seem to be possible. Some complicated reactions may take place during the titration, but it is quite clear, from the results of titrations with ammonium ferrous sulphate solution, that all the manganese is present as permanganate before the titration with arsenite is commenced. [See, further, *J. Soc. Chem. Ind.*, 1919.] W. P. S.

**Separation of Germanium from Arsenic by the Distillation of the Chloride in the Presence of a Chromate.** PHILIP E. BROWNING and SEWELL E. SCOTT (*Amer. J. Sci.*, 1918, [iv], 46, 663—665).—A modification of a method described previously (A., 1917, ii, 546); chromic acid is used to oxidise the arsenic, and the germanium chloride is then distilled from the hydrochloric acid solution. Five c.c. of 10% potassium dichromate solution are sufficient to oxidise 0.25 gram of arsenious acid. A current of carbon dioxide may be passed through the apparatus during the distillation to facilitate the removal of the germanium chloride. If as little as 0.0005 gram of germanium oxide is present, the distillate yields a white precipitate of germanium sulphide on the addition of hydrogen sulphide. [See, further, *J. Soc. Chem. Ind.*, 1918, 785.] W. P. S.

**The Estimation of Phenol and the Three Isomeric Cresols in Mixtures of these Substances.** HARRY MEDFORD DAWSON and CHRISTOPHER ARCHIBALD MOUNTFORD (T., 1918, 113 935—944).

# XI.—*The Sub-acetate and Sub-sulphate of Lead.*

By HENRY GEORGE DENHAM.

IN recent papers the author has shown how lead sub-oxide may be converted into the sub-haloid salts by the action of alkyl haloid vapour (T., 1917, 111, 29; 1918, 113, 249); in the present paper a somewhat similar method has been used for the preparation of lead sub-acetate and sub-sulphate.

In all these experiments, the lead sub-oxide was prepared by the decomposition of pure lead oxalate according to the method previously described (*loc. cit.*). The same precautions have been followed in order to secure thorough preliminary heating of the reacting gases, the vapour being passed through a capillary spiral tube contained in the oven before it came in contact with the sub-oxide. The only modification necessary in the distillation has been that no drying agent was used in the apparatus, and it was necessary to heat electrically all the leading tubes in order to prevent undesired condensation and to secure a steady rate of distillation.

## *Preparation of Lead Sub-acetate.*

Preliminary experiments were carried out with methyl acetate. About 10 c.c. of a carefully dried sample of this substance were distilled through about 0.75 gram of lead sub-oxide, the duration of the experiment being approximately ninety minutes. Analysis of the product indicated that at 310° the sub-acetate decomposes completely, metallic lead being formed, whilst at temperatures much below this, the reaction proceeded too slowly to appear promising. Ethyl acetate behaved similarly, and an experiment was then carried out with acetic anhydride.

Lead sub-oxide mixed with about four times its weight of powdered glass was prepared in two bulbs (for details, see T., 1917, 111, 29), and the apparatus filled with oxygen-free nitrogen. About 8 c.c. of carefully fractionated acetic anhydride were distilled through the bulbs at 195°, as recorded on a standardised platinum thermometer. This slow distillation generally lasted about eighty to ninety minutes. The oven was then cooled to about 180°, and the apparatus was exhausted by means of a Sprengel pump. The bulbs were then sealed off and were available for analysis. By this

procedure, any trace of acetic anhydride could be removed from the bulb without causing any decomposition of the sub-acetate.

One difficulty still remained. Traces of water were found to be retained most tenaciously by the sub-acetate. A few samples which were quite free from moisture were prepared, but in general, although the ratio of lead to acetate in the compound agreed with the theoretical ratio for lead sub-acetate, from 1 to 3 per cent. of water was also present. The presence of the water was repeatedly verified by the action of heat, a liquid which rendered anhydrous copper sulphate blue being fairly readily expelled.

Traces of acetic acid were generally present in nearly all the samples of acetic anhydride used, and this probably accounted for the presence of water in the sub-acetate. However, as the anhydrous and the hydrated sub-acetate showed no difference in solubility and general properties, anhydrous acetic anhydride was used only in certain control experiments.

Found: Pb=77.6, 77.9, 77.9;  $C_2H_3O_2$ =22.3, 22.0, 22.2.

$CH_3CO_2Pb$  requires Pb=77.82;  $C_2H_3O_2$ =22.18 per cent.

In seven experiments made with acetic anhydride containing traces of acetic acid, the average of the analyses was Pb=75.8;  $C_2H_3O_2$ =21.5. There is a possible hydrate of the formula  $(CH_3CO_2Pb)_2 \cdot H_2O$  which contains Pb=75.3 per cent., and it appears probable that where acetic anhydride containing traces of acetic acid is used, the product is the hydrate, containing more or less of the anhydrous sub-acetate. Thus in two experiments, in which the same sample of acetic anhydride was used, after a distillation lasting ninety minutes, the percentage of lead was: (a) bulb 1, 75.4, bulb 2, 75.2; (b) bulb 1, 75.1, bulb 2, 75.2.

#### *Properties of the Sub-acetate.*

In order to obtain evidence of the existence of the sub-acetate, determinations of the conductivity of a saturated solution of the substance and of the normal dehydrated acetate were carried out in absolute alcohol at 25°. The apparatus and method previously described (*loc. cit.*) were again used in order that traces of oxygen might be excluded when the sub-acetate was used. The resistance of the alcohol was 90,000 ohms, whilst that of a saturated solution of the normal acetate was 4100 ohms, and of the sub-acetate, (a) 6100, (b) 6400, (c) 6000 ohms.

As further evidence of the existence of a definite sub-acetate of lead, experiments on the decomposition of the normal acetate and the sub-acetate were undertaken. A sample of the anhydrous

normal acetate was heated in a vacuum and the temperature slowly raised. At  $200^{\circ}$ , a very slow evolution of gas occurred, becoming rather brisker at  $240^{\circ}$ . The temperature was then kept constant and the pump kept in action for nineteen hours. Gas was still very slowly evolved, and it was found that the acetate had scarcely changed colour, and there was a considerable crop of long, white, needle-like crystals which had volatilised out of the bulb into the relatively cooler leading tube within the oven.

A sample of the sub-acetate was then similarly treated. At  $200^{\circ}$ , gas was slowly evolved, the evolution becoming brisker at  $240^{\circ}$ . After seven hours at  $240^{\circ}$ , gas was still being evolved slowly, and a small, volatilised band of white, amorphous, basic material was found outside the furnace, whilst the material in the bulb had undergone a marked change. It was now full of long, needle-like, greyish crystals. This change, from a finely crystalline, bluish-grey substance into a mass of grey, needle-like crystals, was very marked, as, too, was the entire absence of the volatilised, white, needle-like crystals obtained in the decomposition of the normal acetate. The behaviour on heating the different acetates in a vacuum is so different that it would be difficult to maintain the view that the sub-acetate is a heterogeneous mixture of metal and normal acetate, and these results, coupled with the different conductivity of the saturated solutions, must rather be held to confirm the view of the chemical individuality of the sub-acetate. The sub-acetate exhibits the same behaviour towards acids as other sub-salts of lead, namely, it is rapidly decomposed into metal and normal salt.

#### *Lead Sub-sulphate.*

Methyl sulphate was distilled through lead sub-oxide at  $280^{\circ}$  for about seventy-five minutes, the manipulation being similar to that already described for the sub-haloid salts of lead (*loc. cit.*). No difference in behaviour or in appearance was detected in the products prepared from lead sub-oxide or from the sub-oxide diluted with four times its weight of silica. On the other hand, when the distillation was carried out at  $310^{\circ}$ , and the silica omitted, the resulting grey mass was seen under the microscope to contain clusters of white crystals in a dark background, and was clearly heterogeneous.

In the sub-sulphate prepared according to the above method, the lead was estimated by conversion into lead sulphate, and the sulphate by treating the sub-salt with dilute nitric acid, evaporating to dryness, washing out the lead nitrate, and weighing the

residue in a Gooch crucible as lead sulphate. Owing to the presence of traces of carbonaceous matter, the precipitate was generally faintly grey until after gentle ignition.

Found: Pb=81.25, 81.62, 81.30, 81.29;  $\text{SO}_4$ =18.65, 18.56, 18.80, 18.62.

$\text{PbSO}_4$  requires Pb=81.18;  $\text{SO}_4$ =18.82 per cent.

*Properties of the Sub-sulphate.*

The action of acids on the sub-sulphate is similar to their action on the sub-haloid salts. A solution of ammonium acetate when boiled with the substance leaves a deposit of spongy lead. In order to test the chemical individuality of a saturated solution of the salt, determinations of the conductivity in water and alcohol at  $18^\circ$  were made. The resistance of the water was 27,000 ohms, whilst that of a saturated solution of lead sulphate was 3030 ohms, and that of the sub-sulphate was (a) in air, 3100 ohms, and (b) in a vacuum, 3200 ohms.

The difference is so slight that it appears highly probable that there is decomposition into lead and lead sulphate, although no visible change occurred in the appearance of the residue.

The resistance of the alcohol was 90,000 ohms, whilst that of a saturated solution of lead sulphate was 93,000 ohms, and of the sub-sulphate 75,000 ohms.

Although a much more marked difference was obtained, the evidence afforded by the conductivity method was still so inconclusive that further evidence as to the individuality of the salt was sought by investigating the influence of temperature on the sub-sulphate. Were the substance a heterogeneous mixture of lead and lead sulphate, a rise in temperature above the melting point of lead would be expected to cause a pronounced change in the appearance of the finely divided lead. Before heating the sample, some of it was carefully observed under the microscope, and no sign whatever of heterogeneity was noticed, but the whole appeared a uniform iron-grey. The temperature was raised  $120^\circ$  above the melting point of lead for a period of four hours. On cooling, the microscope failed to reveal any change whatsoever in the appearance of the salt. The entire absence of anything in the nature of minute globules of lead certainly supports the contention that this greyish substance is definitely lead sub-sulphate.

*Conclusion.*

(1) Lead sub-acetate has been obtained by the action of acetic anhydride on lead sub-oxide at  $195^\circ$ .

(2) The substance is bluish-grey, and behaves similarly to other sub-salts of lead.

(3) Its solubility in alcohol differs slightly from that of the normal acetate, but the behaviour of the two acetates on heating in a vacuum supports the view of the chemical individuality of the sub-acetate.

(4) The sub-sulphate has been prepared by the action of methyl sulphate vapour on the sub-oxide at  $280^{\circ}$ .

(5) The substance is dark grey; conductivity experiments indicate that it decomposes on solution in water, but it appears more soluble in alcohol than does the normal sulphate.

(6) On heating the substance  $120^{\circ}$  above the melting point of lead, no change in its appearance could be detected or any sign of globules of lead.

In conclusion, the author begs to thank the Walter and Eliza Hall Trust for the facilities placed at his disposal for the prosecution of this work.

THE DEPARTMENT OF CHEMISTRY,  
UNIVERSITY OF QUEENSLAND,  
BRISBANE.

[Received, January 14th, 1919.]

## XII.—*The Synthesis of Ammonia at High Temperatures. Part III.*

By EDWARD BRADFORD MAXTED.

IN previous communications (T., 1918, 113, 168, 386), some account has been given of the formation of ammonia in a rapidly cooled high-tension arc and in water-cooled flames, and evidence has been brought forward to show that the percentage of ammonia in equilibrium with nitrogen and hydrogen, after decreasing with increasing temperature, passes through a minimum value, and at very high temperatures increases with increasing temperature, a result which may also be shown thermodynamically.

A determination of the equilibrium ammonia-content at the temperature of the high-tension arc (*J. Soc. Chem. Ind.*, 1918, 37, 232) gave approximately 1.7 per cent. by volume for the equilibrium percentage at atmospheric pressure under the experimental conditions employed, and yields of ammonia up to 1.5 per cent. could be recovered by suitable cooling.

This reversal in the direction of variation of the equilibrium ammonia-percentage with temperature appears to be sufficiently interesting to justify further study, and it is proposed in the present paper to deal with the formation of ammonia in an arc of larger size and more usual character than those hitherto employed.

For the production of the arc, single-phase, 50-cycle alternating current supplied at a maximum potential of 375 volts was transformed to high tension by means of an oil-immersed static transformer having a step-up factor of 31.5.

It was found easily possible to obtain an appreciable concentration of ammonia by almost any method by which the mixture of nitrogen and hydrogen was brought into contact with the arc flame with subsequent rapid cooling, for instance, by means of a blown arc similar to that used by McDougall and Howles (*Proc. Manchester Phil. Soc.*, 1900, **44**, No. 13) for the synthesis of nitric oxide, but in such cases a considerable proportion of the gas mixture blown into the arc failed to reach the requisite uniform high temperature, and for a preliminary study of the maximum percentage of ammonia formed, as distinguished from the maximum quantity formed with a given expenditure of electrical energy, it was considered preferable to allow the arc to burn freely in the reacting gas mixture and to draw off samples of gas by means of a silica tube of small diameter placed in close proximity to the arc.

The latter part of the present paper was carried out with a view to bringing additional evidence that the formation of ammonia at high temperatures really takes place by the direct union of hydrogen and nitrogen, and not by the subsequent reduction of nitric oxide formed from traces of oxygen in the reacting gases.

It should, further, be stated in this connexion that the mixture of nitrogen and hydrogen employed in all experiments reported both in this and in the previous papers was as far as possible free from oxygen, and in no case contained sufficient of this to account for such secondary formation of any appreciable part of the ammonia obtained.

#### EXPERIMENTAL.

The apparatus employed is shown in the figure. The electrodes *A* and *B* are of platinum, and terminate in small spheres slightly more than 1 mm. in diameter. *C* is a thick-walled capillary silica tube, its upper end being opened out and flattened so as to form a slit approximately 4 mm. long and 1.5 mm. wide. The silica

wall bounding the ends of this was ground away, and in the depressions thus formed at each end of the silica slit, the electrodes rested, the lower part of the tube being circular in section and about 1.5 mm. in internal diameter.

The arc was enclosed in a large inverted flask provided with a side-tube and three-way tap, *D*, for preliminary exhaustion and subsequent admission of the gas to be subjected to the action of the arc, this gas normally passing into the flask at *D* and leaving the system by way of the silica tube already described.

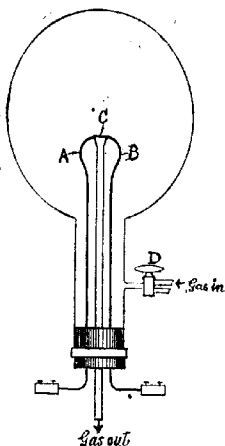
For the following measurements, the current employed for arc formation was limited by the interposition of an adjustable resistance on the low-tension side of the transformer.

The platinum electrodes became quickly white hot and the arc flame burned steadily across the slit, and was, to a certain degree, drawn into the tube by the current of gas. Sufficient cooling for the recovery of the greater portion of the ammonia formed and for the prevention of the fusion of the silica tube was obtained without water-cooling, provided that a thick-walled silica capillary was used and that the arc employed was not too large.

Samples of gas, taken at various rates, were analysed by passage through *N*/10-acid, and in some cases, by allowing a small volume to pass through Nessler's solution, practically identical results being obtained from each method of analysis.

The quantity of ammonia observed is influenced necessarily, not only by the temperature of the arc, but also by heating and cooling factors. With very slow currents of gas, heating to arc temperature occurs satisfactorily, but the ammonia formed undergoes considerable decomposition owing to the slowness with which it leaves the region of maximum temperature. Passage of the gas too quickly through the arc results in imperfect heating, such rapid passage, however, involving rapid cooling, and consequently a more complete retention of the ammonia formed.

It will be seen from table I that the concentration of the ammonia recovered at the ordinary temperature first of all rises rapidly with increasing velocity of passage, then passes a maximum





value, the percentage of ammonia subsequently falling gradually with still greater velocities of passage. This form of the concentration-velocity curve is a necessary result of the nature of the heating and cooling factors discussed above.

The issuing gas, of course, had a strong odour of ammonia at all the rates of flow studied, and the percentages obtained were of the same order of magnitude as those previously observed with small arcs not produced directly by a high-tension current of the usual sinusoidal wave form. For this series of experiments, 0.04 ampere at a potential of 3250 volts was taken for arc-formation.

TABLE I.

*Gas Mixture: Nitrogen, 25 per cent.; Hydrogen, 75 per cent.*

Rate of flow of gas in litres per hour.	Concentration of ammonia per cent. by volume.	Rate of flow of gas in litres per hour.	Concentration of ammonia per cent. by volume.
0.5	0.49	3.4	0.49
0.57	0.6	(3.4	0.45)
0.85	1.2	4.6	0.43
1.14	1.04	6.1	0.40
2.1	0.58	7.5	0.36
(2.1	0.56)	(7.5	0.32)

It appears desirable at this point to discuss the evidence that the formation of ammonia at high temperatures takes place by the direct union of nitrogen and hydrogen, and not secondarily by the reduction of nitric oxide formed from nitrogen and traces of oxygen in the reacting gas. The point is of fundamental importance in any consideration of the variation of the ammonia equilibrium with temperature, and for this reason has been examined in such a way as to place beyond doubt the direct nature of the synthesis of ammonia at arc temperatures.

It may easily be shown from a consideration of the nitric oxide equilibrium, particularly on account of the small partial pressure of the nitrogen in the gas mixture employed, such mixture consisting uniformly of 25 per cent. of nitrogen and 75 per cent. of hydrogen, that a trace of oxygen, amounting to 1 per cent. by volume or less, will not account for the percentage of ammonia obtained, even assuming that all the nitric oxide which can be formed under the conditions of experiment is quantitatively reduced to ammonia. The amount of nitric oxide that can be formed from nitrogen and oxygen at partial pressures of the order mentioned is depressed, by the ratio of partition of oxygen between hydrogen and nitrogen, to a very small fraction of the already

small percentage which may be calculated as capable of being formed from a consideration of the nitric oxide equilibrium only.

In spite, however, of the small order of magnitude of the percentage of ammonia that might be formed secondarily from the traces of oxygen which are always present in commercial gases, it was considered preferable, both for the work described in the present paper and for all measurements of the formation of ammonia at arc temperature previously reported, to employ a gas known to be free from oxygen within the limits of the ordinary methods of analysis.

This gas was prepared in a manner similar to that used by Haber and Van Oordt (*Zeitsch. anorg. Chem.*, 1905, **44**, 341) for their determinations of the ammonia equilibrium at lower temperatures in the presence of a catalyst, by decomposing ammonia by passage through a heated iron tube, the mixture of nitrogen and hydrogen produced being carefully and thoroughly freed from ammonia by treatment with sulphuric acid and compressed for convenience into a previously exhausted steel cylinder by means of a totally immersed compressor of such design as to render impossible any penetration of air to the gas during compression. Each cylinder of nitrogen and hydrogen prepared in this way was carefully tested for absence of ammonia before use, by bubbling a considerable volume through Nessler's solution. The gas-mixture contained certainly less than 0.1 per cent. of oxygen, from which percentage the ammonia capable of being formed secondarily would be negligible, and in any case incapable of accounting for a yield of ammonia of 1 per cent. or more.

In a few preliminary measurements, a gas was used which had been made by the catalytic removal of traces of oxygen from a mixture of commercial hydrogen and nitrogen by passage over a heated metal, but whilst the resulting gas was equally satisfactory from the point of view of the yield of ammonia obtained by passage through an arc, the preparation of an oxygen-free mixture in this way was more troublesome than by the first method.

In addition to employing a gas free from oxygen, it was considered interesting to examine the synthesis at arc temperature under such conditions that the same volume of nitrogen and hydrogen was repassed a number of times through the arc, the ammonia formed at each passage being absorbed and measured. It is obvious that any trace of oxygen would, particularly by reason of the hydrogen present, be removed during the first few passages through the arc, and that the conversion to ammonia of an approximately constant percentage of the gas-mixture during

each successive passage would confirm beyond doubt the direct nature of the synthesis.

The experimental method employed consisted in confining a known volume of an oxygen-free mixture of nitrogen and hydrogen in a graduated vertical glass capillary tube about 1 metre long. The upper end of this tube was fused on to a second, short, horizontal capillary tube containing platinum wire electrodes 0.5 mm. apart, between which a small induction arc, as described in a previous communication, could be formed, this second capillary tube ending in a small absorption pipette filled with dilute sulphuric acid. The lower end of the graduated capillary tube was sealed by means of mercury covered with a small quantity of sulphuric acid, and, by the regulated motion of this seal up and down the graduated tube, the thread of gas could be passed and repassed through the arc as often as desired. An approximately uniform rate of passage was obtained by making the graduated capillary tube one limb of a U-tube and causing the required motion by means of a mercury flow, this being normally regulated so that each double passage through the arc occupied about six minutes when 1 c.c. of the gas mixture was taken for experiment.

Working as above described, the ammonia formed during each upward passage was removed by the small absorption pipette sealed to the other end of the short capillary arc tube, whilst that produced during each downward passage was absorbed by sulphuric acid clinging to the side of the graduated capillary. The arc tube was, of course, not allowed to become wet on account of the danger of fracture, and the thread of gas, after its introduction, passed no joints by means of which penetration of air might occur.

Table II summarises the results obtained in two experiments of this nature, the estimation of ammonia being in this case carried out volumetrically by noting the contraction after each passage. A preliminary small expansion occurred on starting the arc, and passage was only begun after the volume had become more or less constant.

The yields of ammonia are much the same as those previously found for such arcs by other methods of analysis and with more accurate control over the rate of passage. Probably, by reason of the more rapid nature of the cooling, the yields are slightly higher than those obtained with the larger arc described in the first part of the present paper. Each cm. of the graduated capillary corresponded with 0.01 c.c. of gas, so that the volume could be read off with fair accuracy to 0.001 c.c.

TABLE II.

No. of expt.	Vol. of gas passed through arc. c.c.	No. of pas- sages since be- ginning of expt.	Contraction after double passage through arc. c.c.	Percentage of ammonia formed.
1	0.74 (original volume) }	2	0.025	1.7
	0.715	4	0.025	1.7
	0.69	6	0.02	1.5
	0.67	8	0.025	1.9
	0.645	10	0.018	1.4
	0.627	12	0.022	1.8
	0.606	14	0.015	1.2
	0.59	16	0.02	1.7
2	0.825 (original volume) }	2	0.03	1.8
	0.795	4	0.025	1.6
	0.77	6	0.02	1.3
	0.75	8	0.027	1.8
	0.723	10	0.023	1.6
	0.70	12	0.02	1.4
	0.68	14	0.025	1.8
	0.655	16	0.025	1.9
	0.63	18	0.025	2.0
	0.605	20	0.01	0.8
	0.595	22	0.02	1.7
	0.575	24	0.02	1.7
	0.555	26	0.023	2.0
	0.532	28	0.022	2.0
	0.51	30	0.02	1.9
	0.49	32	0.015	1.5
	0.475	34	0.015	1.6

The experimental conditions, including control of rate of flow and the method of analysis, were not suitable for very accurate measurements, but the approximate constancy of the yield of ammonia, and especially the absence of any indication that a normal amount of ammonia is formed during the first passage and little or none during subsequent passages, appears to demonstrate without doubt the direct nature of the synthesis at high temperatures.

[Received, December 23rd, 1918.]

### XIII.—The Effect of some Simple Electrolytes on the Temperature of Maximum Density of Water.

By ROBERT WRIGHT.

ROSETTI (*Ann. Chim. Phys.*, 1867, [iv], 10, 461; 1869, 17, 370) has given a fairly exhaustive account of the early work carried out

on the determination of the temperature of maximum density of water and of a few salt solutions. A considerable portion of this work is due to Despretz (*Ann. Chim. Phys.*, 1839, [ii], **70**, 49; 1840, **73**, 296), and the most important result is embodied in the following law named after that investigator: "The lowering of the temperature of the point of maximum density of water caused by the addition of a solute is directly proportional to the concentration of the latter."

An attempt was made by Rosetti to connect the lowering of the temperature of maximum density brought about by the addition of a solute with the lowering of the freezing point produced by the same cause, but it was found impossible to formulate any general law, for although the ratio of the two lowerings was constant for any given solute at different concentrations, still a different ratio was obtained by the use of a second solute. In other words, whilst the lowering of the freezing point—being connected with the osmotic pressure of the solution—depends only on the concentration of the solute molecules, the lowering of the point of maximum density depends on the nature as well as on the number of dissolved molecules.

Coppet, in a series of researches (*Ann. Chim. Phys.*, 1894, [vii], **3**, 246, 268; *Compt. rend.*, 1897, **125**, 533; 1899, **128**, 1559; 1900, **131**, 178; 1901, **132**, 1218; 1902, **134**, 1208), has determined the molecular lowering of the temperature of maximum density for a number of salts of the alkalis, that is, the lowering produced by a gram-molecule of salt per litre, and the following table contains the more important of his results:

TABLE I.

	Chloride.	Bromide.	Iodide.
Rubidium .....	11.7	13.2	15.6
Potassium.....	11.6	12.8	15.4
Sodium.....	13.2	14.5	17.0
Lithium .....	6.0	7.0	8.3
Ammonium .....	7.2	8.7	11.1

From an examination of these figures, Coppet points out that of the three acid radicles, the iodide has the greatest and the chloride the least effect, and as a general conclusion states that: "Le rapport entre les abaissements produit par le chlorure et le bromure (ou le bromure et le iodure) du même métal est sensiblement le même pour tous les métaux du groupe." The ratio varies between the values 0.78 and 0.91.

From the results of the present investigation, carried out with

monobasic inorganic acids and their salts with univalent metals, it will be shown that the lowering produced by any given salt conforms to a simple general rule, and can, in fact, be calculated from the known lowerings produced by other salts. The results of the measurements are given in table II, which contains the figures obtained for solutions varying in strength between semi- and one-sixteenth-molecular, the normal, or molecular lowerings, being calculated from those of lower concentration.

TABLE II.

*Lowering of the Temperature of Maximum Density of Salt Solutions.*

	<i>M</i> /16.	<i>M</i> /8.	<i>M</i> /4.	<i>M</i> /2.	Molecular lowering.
HCl .....	—	0.7	1.3	2.6	5.2
LiCl .....	—	—	1.4	2.8	5.6
NaCl .....	—	1.6	3.1	6.2	12.4
KCl .....	—	1.4	2.8	5.5	11.0
NH <sub>4</sub> Cl .....	—	1.0	1.8	3.6	7.2
HBr .....	—	0.9	1.8	3.7	7.4
LiBr .....	—	—	1.9	3.8	7.6
NaBr .....	—	1.8	3.7	7.4	14.8
KBr .....	—	1.6	3.2	6.5	13.0
NH <sub>4</sub> Br .....	—	1.2	2.3	4.7	9.4
HI .....	—	1.2	2.2	—	8.8
LiI .....	—	1.2	2.3	—	9.2
NaI .....	1.0	2.0	4.0	—	16.4
KI .....	0.9	1.8	3.7	—	14.8
NH <sub>4</sub> I .....	0.7	1.4	2.7	—	10.8
HNO <sub>3</sub> .....	0.8	1.6	3.1	—	12.4
LiNO <sub>3</sub> .....	—	1.6	3.1	—	12.4
NaNO <sub>3</sub> .....	1.3	2.5	5.0	—	20.0
KNO <sub>3</sub> .....	1.1	2.2	4.5	—	18.0
NH <sub>4</sub> NO <sub>3</sub> .....	0.9	1.8	3.6	—	14.4

It will be seen at once that the results agree with the law of Despretz, the semi-molecular solutions giving twice the depression of the corresponding fourth-molecular. Further, it is obvious that the lowering is not connected with the osmotic pressure, as the values shown for the molecular lowerings of different solutes vary greatly; nor is a consideration of the difference in the degree of ionisation sufficient to account for this abnormality, since the various solutions of any given concentration are practically ionised to the same extent.

The regularity running through all the measurements can readily be seen if the difference between the lowering shown by any acid and, say, its sodium salt is considered. This difference for the four

acids tabulated has the values 7.2, 7.4, 7.6, and 7.6; thus the replacement of the hydrogen ion by sodium causes a practically constant increase in the molecular lowering. A similar increase is found when potassium is used instead of sodium, the average value being 5.75, whilst for ammonium the value is 2.0. Further, the same effect is observed in the case of the acid radicle; thus, the replacement of chlorine by bromine increases the molecular lowering by 2.1, whilst the substitution of iodine for chlorine causes an increase of 3.7.

From a consideration of these results, it is evident that each acidic or basic radicle has its own effect on the lowering of the point of maximum density, and that the effect produced by a salt is equal to the sum of the lowerings caused by the metallic and acidic radicles. Hence, if we take the molecular lowering of hydrochloric acid—which gave the smallest effect of all the substances examined—as standard, we can obtain the molecular lowering of any salt or acid by the addition of two numbers, one corresponding with the acidic and the other with the basic radicle of the salt. It will at once be seen that there is a close resemblance between the above conclusion and Valson's law of moduli, which states that the density of a normal salt solution is the sum of an acidic and a basic effect, and can, in fact, be calculated by adding to the density of a normal solution of a standard substance—ammonium chloride—two figures or moduli, one characteristic of the acidic and the other of the basic radicle of the salt.

The moduli for the lowering of the point of maximum density are given in table III, and the molecular lowering of any salt can be found by adding to the molecular lowering of hydrochloric acid (5.2) the two moduli corresponding with the given salt. For example, the calculated lowering for potassium nitrate would be  $5.2(\text{hydrochloric acid}) + 5.75(\text{potassium}) + 7.2(\text{nitrate}) = 18.15$ , the actual value found being 18.0. Several values for each modulus calculated from different salts are shown in the table, together with the mean value derived from them.

TABLE III.

	Cl.	Br.	I.	NO <sub>3</sub> .	Average.	
Li .....	0.6	0.2	0.4	0.0	0.3	
Na .....	7.2	7.4	7.6	7.6	7.45	
K .....	5.8	5.6	6.0	5.6	5.75	
NH <sub>4</sub> .....	2.0	2.0	2.0	2.0	2.0	
	H.	Li.	Na.	K.	NH <sub>4</sub> .	Average.
Br .....	2.2	2.0	2.4	2.0	2.2	2.2
I .....	3.6	3.6	4.0	3.8	3.6	3.7
NO <sub>3</sub> .....	7.2	6.8	7.6	7.0	7.2	7.2

It should be noted that a similar set of moduli could be calculated from the molecular lowerings given by Coppet, although as a rule his values would not be identical with those tabulated; the results, however, approximate to one another fairly closely considering the difference in the experimental methods employed.

We may next consider the results obtained with the weak mono-basic organic acids in comparison with their highly ionised salts. Formic, acetic, and propionic acids, together with their sodium and ammonium salts, have been examined.

TABLE IV.

	N/8.	N/4.	N/2.	N.
Formic acid .....	—	1.7	3.6	7.2
Na salt .....	1.6	3.2	—	12.8
NH <sub>4</sub> salt .....	—	1.7	3.6	7.2
Acetic acid .....	—	1.8	3.7	7.4
Na salt .....	1.5	3.0	—	12.0
NH <sub>4</sub> salt .....	—	1.6	3.1	6.2
Propionic acid .....	—	2.0	4.0	8.0
Na salt .....	1.5	3.0	—	12.0
NH <sub>4</sub> salt .....	—	1.7	3.4	6.8

The results do not show the normal change, 7.6, which was obtained with strong acids when the hydrogen atom was replaced by sodium, but the difference between the values for the sodium and ammonium salts is constant in all three cases and is identical with that obtained in the case of the inorganic acids. In other words, the highly ionised salts of organic acids behave in the normal manner, whilst the feebly ionised acids themselves are abnormal.

The dibasic acids, with their acid and neutral salts, are also of interest.

TABLE V.

	M/16.	M/8.	M/4.	M.
Sulphuric acid .....	—	3.0	6.1	24.4
NaH salt .....	2.0	4.0	—	32.0
Na <sub>2</sub> salt .....	2.0	4.0	—	32.0
Oxalic acid .....	—	1.5	3.0	12.0
NaH salt .....	—	2.4	—	19.2
Na <sub>2</sub> salt .....	2.0	4.0	—	32.0
Succinic acid .....	—	1.7	3.4	13.6
NaH salt .....	—	2.5	—	20.0
Na <sub>2</sub> salt .....	1.5	2.9	—	23.2

It will be seen that the replacement of one hydrogen atom by



sodium in the two stronger acids gives values approximating to the normal, whilst succinic acid gives a slightly lower value, thus resembling the weak monobasic acetic and propionic acids. In all cases, the replacement of the second hydrogen atom is quite abnormal and differs widely in the three cases. From the normal behaviour of the acid salt, it may be concluded that the ions of sodium hydrogen sulphate consist mainly of  $\text{Na}^+$  and  $\text{HSO}_4^-$ , and not  $\text{H}^+$  and  $\text{NaSO}_4^-$ . It should be noticed that as the greatest concentration examined in these acids was  $M/4$ , the results are not so accurate as with the monobasic acids.

The results obtained for the salts of the bivalent metals show great irregularities, probably on account of the complex ions which are present. For example, the molecular lowering obtained for barium chloride was 24.6 and for barium nitrate 32.8, from which the two values 14.2 and 8.0 are obtained for the modulus of barium. Similar varying results can be obtained from the figures given by Coppet and Müller (*Compt. rend.*, 1902, **34**, 1208) for the lowerings shown by the halogen salts of barium and calcium.

TABLE VI.

	Molecular lowering.		Modulus.
Barium bromide .....	25.14	26.28	10.9
Barium iodide .....	29.24	29.42	11.7
Calcium chloride .....	18.0	18.3	7.8
Calcium bromide .....	20.12	20.93	5.7
Calcium iodide.....	26.09	26.63	8.7

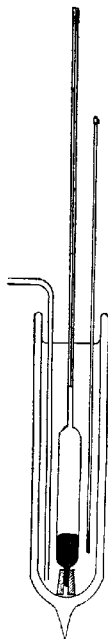
It will be seen at once that there is no regularity comparable with the case of the univalent metals.

## EXPERIMENTAL.

The apparatus employed is shown in the diagram; it consists of a dilatometer with a capacity of about 50 c.c. and fitted with a stem 25 cm. long and of 0.5 mm. bore. To compensate for the change in volume with temperature, a portion of the bulb is filled with mercury; the fraction of the total dilatometer volume thus filled is equal to the ratio between the coefficients of cubical expansion of glass and mercury, so that, on a change of temperature, the expansion or contraction of the metal exactly compensates the expansion or contraction of the bulb, the volume of the latter unoccupied by the mercury thus remaining constant.

The dilatometer is filled by means of a tap funnel and a vacuum

pump. The stem of the dilatometer passes through a rubber cork fitted into the opening of the tap funnel which contains the liquid to be introduced into the dilatometer. The funnel and the attached dilatometer is now inverted and connexion made between it and a filter pump. As the pressure is lowered, the air in the dilatometer bulb bubbles through the liquid in the funnel, and on detaching from the pump, the liquid is forced into the dilatometer by the action of the atmospheric pressure. A second and a third exhaustion are usually necessary, and the last trace of air in the bulb is removed by heating. The dilatometer, with the funnel still attached, is now placed in a vacuum-jacketed vessel filled with brine at about  $5^{\circ}$ , and allowed to cool. When the apparatus has attained the temperature of the surrounding liquid, it is disconnected from the tap funnel and a few shavings of ice are added to the liquid in the vacuum flask; air is then driven through the cooling mixture, so as to stir it until the ice has melted. The apparatus is now left for a quarter of an hour to allow the dilatometer to assume the temperature of the bath; this temperature is then noted, and the level of the liquid in the dilatometer tube measured; the apparatus is again left, and readings are taken at five-minute intervals until the liquid in the dilatometer ceases to contract; this precaution is necessary in order to ensure that the whole apparatus is in a state of thermal equilibrium. A further small quantity of ice is now added so as to lower the temperature a fraction of a degree, and the process repeated. After several additions of ice, the liquid in the dilatometer reaches its point of maximum density, and on further cooling it expands. As this point is approached, the coefficient of expansion of the liquid diminishes, so that it is difficult to determine the exact temperature of maximum density, and the readings given are only accurate to within about  $0.2^{\circ}$ .



After a measurement, the instrument is warmed so as to expel a little of the contents, and is then inverted so that the mercury runs out. This mercury is dried and reserved for the next determination, whilst the rest of the contents of the dilatometer are removed by means of the filter pump. The instrument is then rinsed with the next liquid to be investigated, and, after the re-

introduction of the mercury, it is filled with the solution and the measurement made as before.

A few other points may be noted. The coefficient of expansion of the glass was calculated between the ordinary temperature and  $100^{\circ}$  by filling the instrument with mercury and weighing the quantity expelled when heated in a steam-jacket, whilst the volume of the bulb was measured by filling with water and weighing at a known temperature. The stem of the instrument was not graduated, but the level of the liquid below the upper end was determined by means of a depth gauge fitted with a vernier; by this means, a change of level of 0.1 mm. could be detected, and, moreover, the labour of regraduation of the stem after an accident was avoided.

#### *Conclusions.*

(1) The lowering of the temperature of the maximum density of water produced by the addition of a solute is directly proportional to the concentration of the latter (law of Despretz).

(2) The lowering produced by a highly ionised binary electrolyte is composed of two separate, independent effects, one due to the acid radicle and the other due to the basic radicle of the electrolyte.

(3) The lowering produced by a highly ionised binary electrolyte of molecular concentration can therefore be calculated by the addition of two moduli to the lowering produced by a molecular solution of a chosen standard substance. The chosen standard was *N*-hydrochloric acid, which gives a lowering of 5.2.

(4) The acid salts of the dibasic acids behave normally, but the neutral salts of such acids and the salts of the bivalent metals do not follow any simple rule in their effect on the temperature of the maximum density.

(5) Feebly ionised organic acids show abnormal effects, but the highly ionised salts derived from them behave in the normal manner.

CHEMICAL LABORATORY,  
QUEEN'S UNIVERSITY, BELFAST.

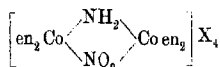
[Received, December 21st, 1918.]

XIV.—*Polar and Non-polar Valency.*

By RAJENDRALAL DE.

IN a paper recently published, Briggs (T., 1917, 111, 267) asks: "What is the valency of cobalt in chloropentammine cobaltic chloride,  $(\text{Co}^{\text{III}}\text{NH}_3)_2\text{Cl}_2$ ?" This question has suggested the view set forth in the present paper.

From the study of the optical properties of the tetraethylenediamine- $\mu$ -aminonitrodicobaltic salts,



Werner (*Ber.*, 1913, 46, 3674) concludes that there is no essential difference between the principal and auxiliary valency bonds. Evidently this conclusion may be applicable only to the bonds within the complex radicle (that is, bonds employed in uniting radicles co-ordinated with the cobalt atom). The bonds outside the complex radicle are employed in combining radicles which exist as ions. Their nature is thus entirely different from that of the former ones. A distinction ought therefore to be maintained between the bonds outside the complex radicle and those within it.

We can find an explanation of the valency outside the complex radicle, which is polar in type, from Sir J. J. Thomson's theory of valency. To understand the mechanism of it, let us picture the structure of an atom derived by Thomson. According to him, the atom consists of corpuscles moving in a sphere of uniform positive electrification, and its valency depends on the ease with which corpuscles can escape from, or be received by, the atom. Difficulties, however, arise in explaining the valencies within the complex radicle in the above manner, they being non-polar in type.

During the disintegration of radioactive substances, the negative charges of electricity are carried by  $\beta$ -rays and the positive charges by  $\alpha$ -rays. The  $\beta$ -rays consist of expelled particles—not atoms of matter, but free atoms of negative electricity or "electrons." An  $\alpha$ -particle, however, consists of two atomic charges of positive electricity combined with a helium atom—a substance inert in the chemical sense. It may therefore be assumed that the positive electricity can have an attraction for the mass itself, even if there be no charge of negative electricity on it. Thomson ("Rays of Positive Electricity and their Application to Chemical Analysis," p. 40) also observes that molecules with positive charges are quite

common, whilst those with negative charges of electricity are very rare. This property which the positive electricity possesses affords an explanation of the phenomena of the valencies inside the complex radicle of a complex salt.

In order to explain the phenomena of the above valencies, we shall consider Rutherford's view as regards the constitution of an atom. According to him, a positive nucleus is situated in the centre, whilst electrons move around it in various concentric rings. We shall conceive this nucleus as having a binding capacity for the radicles which are co-ordinated with a metallic atom in the case of complex salts. It is significant that no positive radicles, such as ammonium, tetramethylammonium, etc., which can exist as cations, have been observed to combine with a metallic atom forming a complex radicle. Negative radicles, such as Cl (chloro-),  $\text{NO}_2$  (nitro-), etc., however, do form a complex radicle with a metallic atom. These negative radicles also carry negative charges of electricity when they exist as anions.

Let us form a picture of the mechanism as conceived above. We have the positive nucleus of the metallic atom (capable of forming a complex radicle) in the centre, and around it there are various concentric rings along which the electrons move. We may assume that adjacent to the outermost ring of electrons constituting the atomic structure there are the neutral molecules, for example,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , etc., or the negative radicles, for example, Cl,  $\text{NO}_2$ , etc., or both these neutral and negative radicles, held by the influence of the positive nucleus of the metallic atom concerned.

Accordingly, in the case of tetraethylenediammine- $\mu$ -aminonitro dicobaltic salts, radicles within the complex radicle may be supposed to be attached to the positive nuclei of its cobalt atoms, and thereby, the valencies within the complex radicle being taken to be all alike, the two cobalt atoms become linked to the two groups in the middle, namely,  $\text{NO}_2$  and  $\text{NH}_2$ , in a similar way.

The conditions favourable to the formation of complex salts may now be stated. The number of concentric rings in the structure of an atom grows large as the atomic weight increases, and thereby, the structure also becomes more complex. According to Rutherford, however (Soddy, "The Chemistry of the Radio-elements," 1914, Part II, p. 39), the mass of an atom is concentrated in an exceedingly small central nucleus. Hence, with the decrease in the atomic volume, only the rings will decrease in size, and the outermost ring will approach nearer to the nucleus. We have already supposed the radicles, co-ordinated with a metallic atom, to be placed adjacent to its outermost ring of electrons and also bound by its nucleus. Evidently, the attraction of the nucleus

for the mass of the radicles would increase where there are possibilities of their being placed near to the nucleus, that is to say, where the atomic volume is small. In fact, metals that are capable of forming complex salts, as, for example, chromium, iron, manganese, cobalt, nickel, copper, ruthenium, rhodium, palladium, osmium, iridium, platinum, gold, etc., are situated on the troughs of Lothar Meyer's atomic volume curve. Here it may also be mentioned that Ephraim (*Ber.*, 1912, **45**, 1322; 1913, **46**, 3103; 1914, **47**, 1828; *Zeitsch. physikal. Chem.*, 1913, **81**, 513, 539; **83**, 196), from his study of the strength of the auxiliary valencies of various metals, has drawn the conclusion that the strength of the auxiliary valencies falls with the increase of the atomic volume of the metal concerned. We thus find a further support for the above assumption.

It will be observed that the metals which form complex salts are mostly found both in the "ous" and the "ic" state of their ionic condition, as, for instance, we have  $\text{Cr}''$  (chromous),  $\text{Cr}'''$  (chromic),  $\text{Co}''$  (cobaltous),  $\text{Co}'''$  (cobaltic), etc. It may also possibly be that the "ous" condition of the metallic ion is more favourable to the formation of a complex radicle. During the reduction of a metallic ion from the "ic" to the "ous" state, there is an alteration in the electric charge of its rings, and the probability is that this alteration is confined to the outermost ring (Soddy, *ibid.*). Evidently, in the "ous" condition of the metallic atom, there is a less number of electrons in its outermost ring. Keeping in view the structure of an atom, it would be natural to expect that, ordinarily, the outer rings of electrons would offer themselves as a shield against the attraction of the positive nucleus for the radicles which may be co-ordinated with a metallic atom. The case is, however, different in its "ous" state, for, there being produced a weakness in the shield, due to a less number of electrons in the ring, the attraction of the nucleus will obtain an opportunity of manifesting itself by forming a complex radicle. It is known that chromic chloride has to be reduced to the chromous state for the preparation of chrom-ammonia salts (Christensen, *J. pr. Chem.*, 1881, [ii], **23**, 54). Similarly, in the preparation of cobalt-ammonia and platinum-ammonia compounds (Gerhardt, *Annalen*, 1850, **76**, 307), the starting materials are the "ous" salts of the metal concerned.

Lastly, it is found that the formation of a complex anion is a more general phenomenon than the formation of a complex cation; for example, there are compounds of the type  $[\text{M}(\text{C}_2\text{O}_4)_3]\text{R}_3$ , where M may be Vd, Cr, Mn, Fe, Co, Rh, Al, As, Sb, or Bi (Werner, "New Ideas on Inorganic Chemistry," p. 115, ed. 1911). It

seems possible that there is a connexion between the increase of attraction of a metallic atom for these negative radicles (co-ordinated with it) and the cause which occasions the presence of negative charges of electricity on them when they exist as anions.

We have already supposed that the valencies outside the complex radicle are caused by electrons of the outermost ring constituting the atomic structure. These electrons may therefore be termed *valence-electrons*. Obviously, the number of the valence-electrons of a metallic atom corresponds with that of its maximum valencies outside the complex radicle. In the case of the complex metal-ammonia compounds, this maximum valency is exhibited when all the radicles co-ordinated with the metallic atom are  $\text{NH}_3$  or  $\text{H}_2\text{O}$ , and when a negative radicle is introduced into the above complex radicle the number of valencies outside the complex one is decreased (that is, the number of valence-electrons appears to become less). We may call those valence-electrons which seem to have vanished in this way *bound valence-electrons*, and those which have caused the appearance of valencies outside the complex radicle *free valence-electrons*. We may also notice that the maximum number of free valence-electrons (that is, electrons which can escape from a metallic atom, forming a complex cation) is the same as the maximum number of electrons which can be received by the atom in addition to its own valence-electrons, when it forms a part of a complex anion. For illustrating this point, we may cite the compounds: (i)  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ , where the complex radicle is a trivalent cation, (ii)  $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ , where the complex radicle is a trivalent anion, and (iii)  $[(\text{NH}_3)_5\text{Co}(\text{NO}_2)_3]$ , a non-electrolyte. In the third compound, no electron has escaped or been received by the metallic atom, but all the three valence-electrons, along with the three univalent negative radicles, have been bound by its positive nucleus. Regarding the question at hand, namely, that of the number of valencies in chloropentamminecobaltic chloride, it may be said that here the cobalt atom contains three valence-electrons—one is bound along with the univalent chloro-radicle co-ordinated with cobalt, and the remaining two have caused the appearance of valencies of polar type outside the complex radicle. Besides these three valence-electrons, the metallic atom possesses six valency bonds of non-polar type caused by the attraction of its positive nucleus.

The structure of the complex radicle as conceived above explains also the phenomenon of the directional nature of the auxiliary valency bonds, indicated by the stereoisomeric compounds of complex metal-ammonia salts, for the nucleus, being centrally placed in the structure of an atom (metal), has an advantage in exerting

its attraction along different directions, which the electrons moving in their orbits cannot possibly have. The assumption of the nuclear attraction, however, need not be confined to these cases of complex derivatives alone. The phenomena of non-polar valency may, in general, be considered to have arisen from this attraction.

The kind of valency exhibited in organic compounds is a typical non-polar one. If we compare the valencies of the carbon atom with those of metallic ones, employed in co-ordinating radicles with them, we find that both these two kinds are non-polar and directional in nature (shown by the stereoisomerides of the carbon compounds and those of complex metal-ammonia derivatives). This similarity in their character may indicate the probability of their being brought about by the same cause, namely, by the attraction of the positive nucleus of an atom. The assumption receives further support from the small atomic volume of carbon (as shown in Lothar Meyer's atomic volume curve). It has already been supposed that the attraction of the nucleus for radicles should increase as the atomic volume decreases, and this should tend to a maximum when the volume becomes very small.

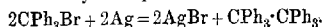
Nernst is of opinion that the forces by which the carbon atoms in a crystal of diamond are held together are identical with the attraction of its four valencies called into play in the formation of organic compounds, that is to say, "the forces of cohesion are identical in nature with the forces of chemical affinity" ("The Theory of Solid State," p. 6). The cohesive forces are found to increase with the decrease of the atomic volume of elements. They may therefore arise from the very same nuclear attraction of atoms mentioned before. An inspection of the behaviour of carbon and its compounds might help in giving some light in this direction.

In the process of the synthesis of diamond, an immense pressure is brought about by the contraction of iron in which carbon has been dissolved. Evidently, for effecting union (that is, saturation of the valencies of carbon atoms), the atoms are required to be brought very near to one another. It may also be noted that in the case of the carbides of metals, the carbides  $\text{Li}_2\text{C}_2$ ,  $\text{CaC}_2$ , etc., where the metals are of large atomic volumes, are decomposed by water, whilst the carbides  $\text{Cr}_3\text{C}_2$ ,  $\text{Cr}_7\text{C}_3$ , etc., where the metals in combination are placed on a trough in the atomic volume curve (that is, are of small atomic volumes), form stable compounds. Taking into consideration that the mass of an atom is concentrated in an exceedingly small central nucleus in the structure, it seems possible that carbon atoms would exert only a very feeble attraction when placed a little apart or when combined with metals of large atomic volumes. The various rings of electrons around the



nucleus, which have already been compared to shields, may also occasion a further hindrance in their union.

Further light will be thrown on the above if the following view is taken of the constitution of triphenylmethyl. It is found that in solution triphenylmethyl has a molecular weight corresponding with the formula  $(CPh_3)_2$  (Gomberg and Cone, *Ber.*, 1904, **37**, 2033). This is what may be expected from its mode of preparation:



As the compound is very reactive, even at a low temperature, it has been assumed that it is rather a derivative of tervalent carbon. Exposure to the air, even for a very short time, is sufficient to transform it into a peroxide of the constitution  $CPh_3 \cdot O \cdot O \cdot CPh_3$ .

We may, however, represent the constitution of triphenylmethyl as  $CPh_3 \cdots CPh_3$ . The weak attraction between the two carbon atoms is shown by the dotted line. The feebleness of their attraction may be due to the inability of the carbon atoms to approach very near to each other on account of the hindrance caused by the large phenyl groups attached to them. The hindrance referred to may be of the type similar to that of steric hindrance (Wegscheider, *Monatsh.*, 1895, **16**, 148), and their reactivity may be due to the possibility of their drawing small atoms very near to them. Viewing the constitution given for the oxidation product, it is seen that by the intervening of two oxygen atoms the large radicles have been placed apart, and by the union of the two carbon atoms with two oxygen atoms (small indeed compared with the triphenylmethyl radicle) a stable compound has been formed.

According to our assumption, radicles bound by the positive nucleus should not show any polar character. Although the valency of carbon is ordinarily non-polar, there are a few organic compounds where it seems to function as polar, as, for instance, in hydrogen cyanide and in organic acids, where we have the radicles  $\cdot C \equiv N$  or  $\cdot N \equiv C$  and  $R \cdot CO_2 \cdot$  respectively, besides hydron. There are also sodium acetylide,  $CH \equiv CNa$ , silver acetylide,  $C_2Ag_2$ , and cuprous acetylide,  $C_2Cu_2$ , where the hydrogen atoms of acetylene have been displaced by metallic atoms. In order to explain this anomaly, we may consider Sir J. J. Thomson's observation that "when the discharge tube contains such gases as  $CH_4$ ,  $CO_2$ ,  $CO$ , where there are no bonds between two carbon atoms in the molecule, we find negatively charged carbon atoms, but no negatively charged molecules. When, however, we use compounds such as acetylene,  $HC \equiv CH$ , ethylene,  $H_2C \equiv CH_2$ , or ethane,  $H_3C \cdot CH_3$ , where, according to the usual interpretation of the constitution of these substances, there are bonds between carbon atoms in the molecule, then we find molecules as well as atoms of carbon with the negative

charge" (*loc. cit.*). He is also of the opinion that on account of the unsaturated valencies of the carbon atoms in the molecule, it has been possible for the negative corpuscles to become attached to them (*ibid.*). A similar explanation may be applicable in the above cases. In them, more than one bond of carbon has been occupied with the other element combined with it, and a corpuscle received from an adjacent hydrogen atom may become attached to the remaining part of the compound, thus giving rise to their polar character.

Compounds such as  $\text{LiH}$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , etc.,  $\text{Ni}(\text{CO})_4$ ,  $\text{Co}_2(\text{CO})_8$ , etc., and also groups of atoms forming radicles, such as  $\text{CO}_2$ ,  $\text{NO}_2$ ,  $\text{SO}_2$ , etc., being formed by non-polar valencies, may have their origin in the nuclear attraction. We may also ascribe the forces by which atoms and molecules in a crystal are held together to the same attraction. These forces have been supposed to be caused by residual valency, which has also been assumed to bring about the solution of a substance in a solvent (Baly, "Spectroscopy," 1912, p. 487). The phenomena of solution should necessarily be considered to be due to the same attraction of the nucleus. In these cases, the size of the molecules may account for the feeble character of their binding. Lastly, all catalytic substances which are employed in gaseous reactions may be supposed to owe their catalytic action to the positive nuclei of the atoms in them. Indeed, the study of the dissociation of the hydrogen molecule into atoms, and other similar studies, have convinced Langmuir (*J. Amer. Chem. Soc.*, 1916, **38**, 2221) that prior to the dissociation, absorption of hydrogen by tungsten wire, due to its secondary valency, does take place. We see, therefore, that the nuclear attraction plays a great part in all chemical phenomena.

Regarding the number of valencies of the non-polar type for different elements, it may be noted that carbon (placed in the first trough of Lothar Meyer's atomic volume curve) has four valencies, whilst other elements (placed in subsequent troughs of the curve) generally have six. In the case of the complex platinum-ammonium salts, however, the derivatives of the platinous salts, for example,  $[(\text{NH}_3)_4\text{Pt}]\text{Cl}_2$ , tetra-aminoplatinous chloride, show the number of auxiliary (non-polar) valencies to be four, whilst those of the platonic salts, for example,  $[(\text{NH}_3)_6\text{Pt}]\text{Cl}_4$ , hexa-aminoplatinic chloride, the number is six. The increase of two non-polar valencies in the latter case has been attended with an increase of two polar ones. Also the directions of these valencies, in the former case, lie in a plane, whilst in the latter case there are two additional directions lying in the same line perpendicular to the above plane. Whether and how the electrons constituting

the atomic structure influence the number and directions of the non-polar valencies of different elements awaits further study.

My best thanks are due to Prof. P. C. Rây for his kind help and encouragement.

PRESIDENCY COLLEGE, CALCUTTA.  
ISLAMIA COLLEGE, PESHAWAR, INDIA.

[Received, October 2nd, 1917.]

### XV.—*The Interaction of Stannous and Arsenious Chlorides.*

By REGINALD GRAHAM DURRANT.

THE action of stannous chloride on arsenious oxide dissolved in hydrochloric acid was first noticed by A. Bettendorf (*Sitzungsber. Niederrhein. Ges. Bonn*, 1869, 128\*) two years after his discovery of yellow arsenic [*ibid.*, 1867, 67, and (full paper) *Annalen*, 1867, 144, 110].

He records the formation of a voluminous, brown precipitate which proved to be arsenic (96—99 per cent.) with traces of non-removable tin. He showed that the rate of precipitation increases with ascending specific gravity of the arsenious solution. By dissolving magnesium ammonium arsenate in acid he made a standard solution and treated this with stannous chloride in varying dilutions of hydrochloric acid. (His figures will be quoted later on.) From these results he showed that the reaction is extremely delicate. It may be utilised for determining arsenic in sulphuric or crude hydrochloric acid. During a distillation with the latter he observed a faint yellow coloration, which disappeared after a few hours. Arsenic was found to be present in this sample of hydrochloric acid, but he was unable to prove that the fading coloration was due to arsenic.

The observation of this yellow coloration has decided me to record a very remarkable yellow precipitate which, in 1914, I exhibited as "yellow arsenic" to the Science Masters' Association in London. The precipitate was quite bright yellow at first, and was always kept in the dark except when shown for short periods. After a year

\* I am indebted to Dr. Hatchett Jackson who recently procured me a rescript of this paper from the Bodleian Library.

it had become a dull mustard colour, being still in the original, well-corked flask and surrounded by the original solution (a mixture of arsenious and stannous chlorides in nearly normal hydrochloric acid). Every effort was made to repeat this, but in vain. When filtered off, the precipitate appeared very dull and shrunken on the paper. After washing, it was specially tested for sulphur (since arsenious sulphide is yellow), but no trace of sulphur was found. The presence of arsenic was proved.

On many points I find that my observations have been anticipated by Bettendorf, in particular the possibility of making the reaction a means of differentiating arsenic from antimony.

#### EXPERIMENTAL.

##### *The Nature of the Arsenic Precipitated.*

Arsenic is probably in a colloidal state before it is precipitated, for (i) the precipitate invariably contains a trace of tin salts (chloride as well as tin), and this cannot be removed completely by prolonged washing; (ii) two similar solutions (reactants, 0.44*N*- and 3*N*-hydrochloric acid) were left corked for two days and remained quite clear. One was then diluted with an equal volume of water. After four days both had deposited arsenic. A third solution at the start was made up to the lower of the above concentrations and remained perfectly clear for twenty-five days.

The appearance of solid arsenic is always preceded by a pale buff tint; from this a buff-brown precipitate falls, and is best observed from such admixtures as yield a very slow deposit. If this deposit, after washing, is immediately shaken with carbon disulphide, arsenic is found to be dissolved. The yield is rather greater if carbon disulphide is shaken violently with the two chloride solutions while they are interacting. On five occasions small, pale particles were observed to rise from the clear disulphide solution during spontaneous evaporation. They moved about rapidly, congregating in the centre of the surface, then darkened, and finally settled on the bottom of the dish in the form of grey arsenic.

Erdmann (*Zeitsch. anorg. Chem.*, 1902, **32**, 453) obtained arsenic soluble in carbon disulphide by reducing arsenious oxide with zinc dust in the presence of the solvent. Very small quantities were obtained by the author in this way.

These results, and those referred to in the Introduction, indicate that the very earliest deposit of arsenic is of the yellow type, but that unless certain unascertained conditions obtain, the yellow variety spontaneously becomes brown or grey.

*Nature and Conditions of the Reaction.*

The obvious equation is  $2\text{AsCl}_3 + 3\text{SnCl}_2 = 3\text{SnCl}_4 + 2\text{As}$ , and when weights of the reactants, corresponding with this equation, are placed in hydrochloric acid of sufficiently high concentration the action reaches completion in a few hours. With other weights excess of either reactant corresponds with calculation. The action has been proved to be irreversible, for, if finely divided arsenic is boiled with solutions of stannic chloride in the presence of hydrochloric acid of varying concentration, in no case does the resulting solution give any precipitate with mercuric chloride.

A very careful experiment was made in order to ascertain if the anhydrous chlorides react.

Fresh arsenious chloride was so arranged that on movement of the handle of an air-pump some would drop on to dry, powdered stannous chloride—also under the receiver. After four days' final drying with phosphoric oxide, the experiment was made. Beyond the faintest darkening no discoloration occurred. On exposure to air a distinct brown colour overspread the powder, and when a drop of water was added a heavy crusting of arsenic appeared immediately.

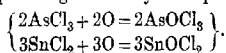
*General Method of Estimating the Rate of Progress of Action.*

Separate solutions containing known weights of the two chlorides were made up in known concentrations of hydrochloric acid. Portions of these solutions were evaluated separately by means of standard permanganate. The results were found to agree with the known concentrations. All stock flasks were re-tested from time to time.

Small dry flasks were placed in a large thermostat, and into these definite volumes of both chloride solutions were introduced by separate pipettes.

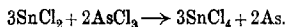
After definite intervals water was added. The dilution effectively stops the action. The contents of each flask were then filtered and uniformly washed. Standard permanganate was used to determine the amounts of stannous and arsenious chlorides remaining in the filtrates and wash-water.

The action of the permanganate may be expressed:



As the filtrates required less permanganate than did the sum of

the separate solutions, the deficit became a measure of the change which had occurred. Two-fifths of this deficit were due to the precipitation of arsenic and the rest to the formation of stannic chloride in the reaction:



*Errors.*—The sources of error in this process are: (1) imperfect washing, (2) loss by adsorption, (3) oxidation of stannous chloride due to access of air.

The two first, considered together, were found to give rise to an error probably less than 2 per cent.

The third source of error was almost eliminated by keeping the stock solutions of stannous chloride in a well-corked flask and by introducing carbon dioxide immediately after use on every occasion. In the same way the reaction took place in small, corked flasks in which the air was displaced by carbon dioxide. Air had access only during the process of filtration.

*Calculations.*—The recognised integration equations for first and second order reactions were applied to a large number of determinations. In no case did the velocity constants conform to the second order. The results quoted are from the first-order equation,  $\frac{1}{t} \log \frac{a}{a-x}$ , where  $a=100$ ,  $x$ =percentage of change, and  $t$ =time in minutes. Hence the mean value of  $k$  for each set of experiments represents a special figure by which the relative speeds may be compared.

TABLE I.

$t=12.5^\circ$ . Normalities:  $\text{SnCl}_2=0.507$ ,  $\text{AsCl}_3=0.584$ ,  $\text{HCl}=6.06$ .  
 $N/4$  Permanganate used. Complete oxidation should correspond with a deficit of 45.6 c.c.

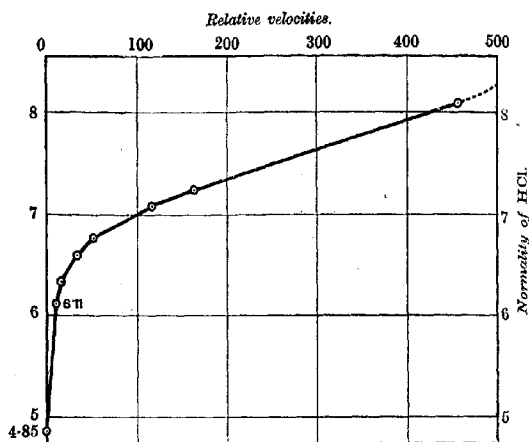
Interval, minutes.	Deficit, c.c.	Percentage change.	$k \times 10^3$ .
2	3.65	8.0	1.81
5	9.3	20.8	2.03
8	16.65	36.5	2.46
10	17.05	[37.4]	[2.03]
12	26.25	57.5	3.09
15	29.4	64.5	3.00
20	33.85	74.2	2.94
30	38.45	84.3	2.68
40	40.1	87.9	2.29
50	40.8	89.5	2.06
65	41.9	91.9	[1.68]
100	42.85	93.9	2.21
120	43.6	95.6	2.97
180	43.9	96.3	2.40

Mean 2.57

Various further unimolecular values of  $k$  were obtained. These were found to depend more on the concentration of hydrochloric acid than on anything else. The results made it possible to choose suitable concentrations for systematic study.

*Influence of Hydrochloric Acid.*

In the following experiments 0.2500 gram of stannous chloride



Relative velocities of the reaction:  $3\text{SnCl}_2 + 2\text{AsCl}_3 = 3\text{SnCl}_4 + 2\text{As}$ , due to alterations of hydrochloric concentration. See Table II.

Temperature =  $12^\circ$ .

acted on the equivalent weight of arsenious chloride in each case. The concentration of hydrochloric acid alone was varied.

TABLE II.

$t = 12^\circ$ . Reactant Normality = 0.298.

Normality of HCl.	Range of change, per cent.	Mean value, $k \times 10^2$ .
10.09	40—61	21.2
8.10	36—64	13.5
7.26	32—63	4.76
7.09	34—78	3.43
6.77	13—63	1.46
6.60	21—69	0.944
6.34	28—64	0.436
6.11	41—53	0.293
4.85	19—53	0.0293

The curve, obtained by plotting these relative velocities against concentration of hydrochloric acid between  $4.85N$  and  $8.10N$ , is exceedingly regular. Its sharpest curvature is in the neighbourhood of  $6.5N$ . If the regularity persisted up to the limit of possible hydrochloric acid concentration (about  $10.3N$ ) then the velocity at  $0.09N$  would be well over a thousand times what it is at  $4.85N$ —as measured it is only 723 times as great.

*Influence of Simultaneous Change in Concentration of Reactants.*

In all these experiments, the concentration of hydrochloric acid remained constant at  $6N$ .  $t=18.4$ .

Four 250 c.c. flasks— $A$ ,  $B$ ,  $A_1$ ,  $B_1$ —contained, respectively,  $\text{SnCl}_2=1.74N$ ,  $\text{AsCl}_3=1.76N$ ,  $\text{SnCl}_2=0.87N$ ,  $\text{AsCl}_3=0.88N$ .

The concentration of hydrochloric acid became  $6N$  as soon as the mark in each flask was reached.

Equal volumes from  $A$  and  $B$  were mixed in six small flasks, and after 4, 6, 8, 10, 12, and 14 minutes, respectively, their filtrates were titrated with  $N/4$ -permanganate.

In the same way, equal volumes from  $A_1$  and  $B_1$  were treated from seven flasks after 24, 32, 48, 64, 80, 96, and 112 minutes, respectively, the filtrates being titrated with  $N/8$ -permanganate.

In each set, the range of progress was from 30 to 70 per cent.

For  $AB$  set, mean value  $k \times 10^2 = 4.33$ .

For  $A_1B_1$  set, mean value  $k_1 \times 10^2 = 0.557$ .

Hence  $k/k_1 = 7.77$  for the range between 30 and 70 per cent. The range between 30 and 40 per cent., however, gave  $k/k_1 = 5.5$ .

*Effect of altering the Concentration of Each Reactant Separately.*

Preliminary work had appeared to show that arsenious chloride reacts as a second, and stannous chloride as a first power.

The following solutions were prepared, tested, and preserved with all possible care. Five c.c. of stannous chloride solution reacted with 5 c.c. of arsenious chloride solution in each case. The washing was strictly uniform, so that errors hence arising were similar.

The mean results, (2) and (4) in the following table, are fairly concordant. Those of (3) and (5) are more so.

The results from comparison of (1), (4), and (5) confirm the preliminary work with respect to arsenious chloride, which is seen to react as a second power.

The period preceding the first appearance of arsenic, from a solution of its chloride at one-fifth the original concentration, was noticed to be just about twenty-five times as great as it had been.



TABLE III.

HCl = 6*N*.  $t = 16.7^\circ$ .

(1) <i>N</i> -AsCl <sub>3</sub> acting on <i>N</i> -SnCl <sub>2</sub> in 12 minutes required c.c. <i>N</i> /4-KMnO <sub>4</sub>			Required by theory after 33.3 per cent. change.
Mean of 2 readings	27.85		26.66
(2) <i>N</i> -AsCl <sub>3</sub>	on <i>N</i> /2-SnCl <sub>2</sub> in 12 minutes	23.3	23.3
(3) <i>N</i> -AsCl <sub>3</sub>	" on <i>N</i> /3-SnCl <sub>2</sub> in 12 minutes	20.8	22.2
(4) <i>N</i> -SnCl <sub>2</sub>	" on <i>N</i> /2-AsCl <sub>3</sub> in 48 minutes	22.55	23.3
(5) <i>N</i> -SnCl <sub>2</sub>	" on <i>N</i> /3-AsCl <sub>3</sub> in 108 minutes	20.9	22.2
	"		

This suggested a method of working to a standard tint, as in Nesslerisation; moreover, the method compares the earlier stages of action on which calculations are more appropriately based.

The tint used in table IV was obtained by the action of hydrogen sulphide on a very dilute solution of lead acetate.

TABLE IV.

HCl = 6*N*.  $t = 10^\circ$ .

Times to reach Standard Tint are given in Seconds.

Stannous chloride.	Arsenious chloride	→ <i>N</i> . → <i>N</i> /2. → <i>N</i> /3.			Total.	Ratio.	$\sqrt{c}$ .
<i>N</i>		30	110	260	400	1.0	1.0
<i>N</i> /2		40	160	360	560	1.40	1.41
<i>N</i> /3		50	220	460	730	1.82	1.73
Total		120	490	1080			
Ratio		1	4.08	9			
$1/c^2$		1	4	9			

A similar set of nine readings referred to another artificial standard tint gave ratios: powers of AsCl<sub>3</sub>, 1:4:3:10:0; powers of SnCl<sub>2</sub>, 1:1:37:1:80.

The *N*/3-stannous chloride solution, on testing, was found to have deteriorated slightly; the others had not.

A solution of *N*/4-stannous chloride was made. Using *N*/2-arsenious chloride against *N*/2- and *N*/4-stannous chloride, the times were 230 and 320 seconds respectively, giving a ratio 1/1.39, again closely approaching  $1/\sqrt{2}$ .

The results here given lead to the conclusion that in this reaction arsenious chloride reacts as a second power and stannous chloride reacts to the power of the square root of its concentration.

The figure 5.5, noted in the last paragraph for the change between 30 and 40 per cent., is quite consistent with the results here given, since  $2^2 \times \sqrt{2} = 5.64$ .

The action of stannous chloride to the square root of its concentration is also in agreement with Bettendorf's figures (*loc. cit.*, 1869). He took 0.001 gram of arsenic dissolved in 1 c.c. in each of five experiments, adding this to a definite amount of stannous chloride solution in the presence of hydrochloric acid. In the four last experiments he also added 50, 100, 200, and 400 c.c. of hydrochloric acid (presumably of similar concentration).

An immediate precipitate occurred in the first experiment, and the arsenic appeared in 5, 8, 12, and 20 minutes, respectively, in the others.

Neglecting 1 c.c. of arsenious chloride + an unknown volume of stannous chloride solution originally taken, his concentrations were 1:2:4:8, his times were 1:1.6:2.4:4, figures which approach 1:1.41:2:2.83, but exceed them in each case, because of the influence of the second power action of arsenious chloride, present in very small relative amount. (His experiments were made to show the delicacy as regards arsenic.)

#### *Effect of Dilution with Water.*

The stock solutions, when mixed, were at concentrations  $\text{HCl} = 6N$  and reactants each at  $0.88N$ . When undiluted, this mixture produced 70 per cent. change in twelve minutes. The dilutions (in ten steps) finally brought all the concentrations to one-third of the above.

The hydrochloric acid normalities, and the state of change after five days are noted in each case.  $t = 16^\circ$ .  $6N$ ,  $5.45N$ , and  $5N$  had reached complete change.  $4.61N$  89 per cent.,  $4.29N$  59 per cent.,  $4N$  24.4 per cent.,  $3.75N$  14.2 per cent.,  $3.53N$  5.6 per cent.,  $3.3N$  3 per cent.,  $3N$  1 per cent., and  $2N$  no change and no subsequent sign of action after 29 days. This retarding action was made use of in all previous experiments when titrations with permanganate were made, the dilution with water being sufficient to reduce the concentration to one-third or less.

#### *Summary.*

(1) There is evidence that arsenic in process of precipitation is partly soluble in carbon disulphide. In certain circumstances, arsenic may appear as a yellow deposit.

# 142 INTERACTION OF STANNOUS AND ARSENIOS CHLORIDES.

(2) The anhydrous chlorides (arsenious and stannous) do not interact.

(3) Acceleration of the action is caused chiefly by increase in the concentration of hydrochloric acid, next by that of arsenious chloride, and least of all by that of stannous chloride. Arsenious chloride acts as a second power and stannous chloride to the power of the square root of its concentration.

## Conclusions.

The various phenomena and the figures given can be accounted for on the hypothesis that this action is between chloride ions, arsenious ions, and the stannous complex  $H_2SnCl_4$ .

Stoppage by dilution must be due to the destruction of arsenious ions by hydrolytic action.

(1) Chloride ions proceed partly from arsenious chloride and partly from hydrochloric acid, and they act as a first power.

The velocity constants found in table II are thus explained.

HCl normality.	$k \times 10^4$ .	$k/k$ .	$Cl'/Cl$ .
10.09	21.2	.....	7.09
8.10	13.5	.....	3.55
7.25	4.76	.....	1.54
7.09	3.43	.....	2.08
6.77	1.46	.....	1.58
6.60	0.944	.....	1.88
6.34	0.438	.....	2.66
6.11	0.293	.....	5.28
4.85	0.0293	.....	
Aggregate	25.04		25.66

In the last column, the numerator gives the sum of chloride ions due to arsenious chloride and those due to increased hydrochloric acid concentration; the denominator is constant, and represents the chloride ions due to the 0.298*N*-arsenious chloride, which is constant throughout the table. In the lower portion of the table, the arsenious chloride is not wholly ionised; in the upper portion, hydrochloric acid becomes less ionised at its higher concentrations. As is seen, the aggregate acceleration is directly proportional to the increase of chloride concentration.

(2) Positively charged arsenious ions also act as a first power. Arsenious chloride as a whole appears, therefore, to act as a second power.

(3) That a compound of hydrochloric acid and stannous chloride exists in solution was indicated by Young (*J. Amer. Chem. Soc.*, 1901, **23**, 21, 450), and several stannochlorides, corresponding with

the formula  $M_2SnCl_4$ , have recently been described (compare Druce, *Chem. News*, 1918, 117, 193). In the reaction, this complex must be decomposed in order to produce stannic chloride, and this decomposition may account for the complex acting to the power of the square root of its concentration.

According to accepted theory, the order of a reaction is governed by the slowest reactant. The order here is unimolecular, and the slowest reactant is this complex. Essentially the action consists in the disintegration of the complex by circumambient ions.

THE COLLEGE,  
MARLBOROUGH.

[Received, July 30th, 1918.]

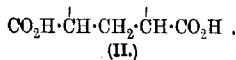
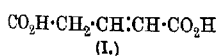
# *XVI.—Experiments on the Elimination of the Carboethoxyl Group from Tautomeric Systems. Part I. Derivatives of Indene.*

By CHRISTOPHER KELK INGOLD and JOCELYN FIELD THORPE.

HERE have been placed on record within recent years (T., 1905, 37, 1669, 1685; 1911, 99, 2187, and subsequent papers of the same series) a number of experiments dealing with substances possessing the kind of tautomerism which is associated with the three-carbon system



These experiments have for the most part dealt with glutaric acid and its alkyl derivatives, and the conclusion was reached that glutaric acid itself has the symmetrical or "normal" structure (II), the unsaturated or "labile" form (I) being too unstable to have any but a momentary existence.

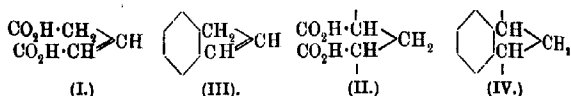


When, however, alkyl groups were introduced into the three-carbon system, the unsaturated form was found to become very noticeably more stable with increasing weight of the substituents.

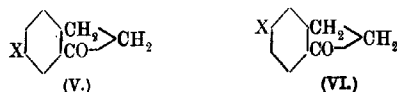
It was thought desirable to extend these investigations to substances possessing the three-carbon tautomeric complex, but containing groups other than carboxyl attached to its terminal carbon atoms—preferably to some substance in which the possible

symmetry of the molecule could be tested without in any way tampering with the three-carbon system.

Such a substance presents itself in the hydrocarbon indene, the analogy of which to glutamic acid becomes apparent when the formulæ are written together, thus:



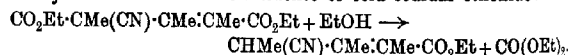
It was hoped originally that the accuracy either of III or of IV might be proved by preparing solid substituted indenenes from  $\alpha$ -hydrindones of the types V and VI.



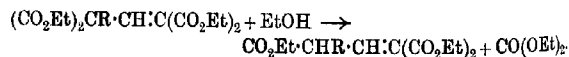
If the unsubstituted three-carbon system of the indene nucleus is symmetrical, as would be expected from analogy to unsubstituted glutamic acid, the ketones V and VI should yield the same indene, whilst, if unsymmetrical, two different indenenes should result.

We have not yet been able to elaborate methods leading to the preparation of suitable ketones of the types V and VI in sufficiently large quantities to ensure the success of this method of attack. In the meantime, however, we have made use of more easily available materials to obtain evidence bearing on the subject, and in particular to investigate a reaction which has been repeatedly observed among esters of the glutamic series, and appears to be peculiar to tautomeric compounds.

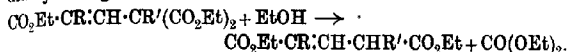
In 1905 the observation was made (Rogerson and Thorpe, T., 1905, **87**, 1702) that ethyl  $\gamma$ -cyano- $\alpha\beta\gamma$ -trimethylglutaconate readily passed into ethyl carbonate and ethyl  $\gamma$ -cyano- $\alpha\beta\gamma$ -trimethylcrotonate under the influence of cold sodium ethoxide:



Since that time, fairly extensive use has been made of this reaction in the preparation of a series of alkylated glutamic esters (Thole and Thorpe, T., 1911, **99**, 2187). Thus the monoalkylated products derived from Conrad and Guthzeit's yellow sodium compound (*Annalen*, 1883, **222**, 259) yielded ethyl carbonate along with tribasic esters:

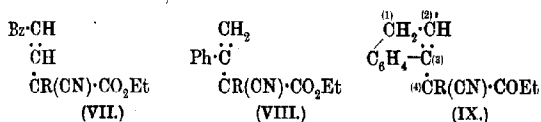


The tribasic esters did not decompose when treated with excess of the same reagent, but on further alkylation gave  $\alpha$ -dialkyl derivatives, which reacted readily to form ethyl carbonate and dialkylated glutaconic esters:



The study of these and similar cases led to a generalisation regarding the determining cause of these reactions. They have always been found to be peculiar, in substances of the glutaconic type, to those in which all the terminal hydrogen atoms of the three-carbon system have been substituted. It was therefore inferred that the tendency in such cases to acquire the hydrogen atom necessary to enable the substance to pass into its tautomeric form is such that a carbethoxyl group readily becomes detached from the molecule and replaced by an atom of hydrogen under the influence of a suitable reagent. We shall have occasion more than once to make use of this general rule.

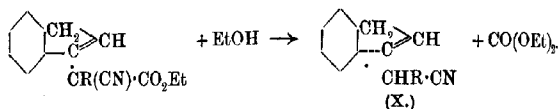
The ethyl carbonate reaction is therefore very closely bound up with the tautomerism of the three-carbon system. One would not therefore expect derivatives of vinylacetic acid, such as those represented by formulæ VII and VIII, in which the double bond would be purely static, to exhibit this reaction to any marked degree.



It was therefore decided to prepare an ester of the type IX and investigate its behaviour towards cold sodium ethoxide. The similarity with VII and VIII is clear. If the double bond in the ester IX really possesses the same stable character, we should for similar reasons expect it to be unreactive. This conclusion is in agreement with the generalisation above cited; for if the three-carbon system (1), (2), (3) (see formula IX) in the indene ring is non-tautomeric and the double bond quite static between the carbon atoms (2) and (3), then, since this same double bond enters also into the three-carbon system (2), (3), (4), the latter must be non-tautomeric as well. Its normal form would clearly be incapable of existence, since the central carbon atom (3) is rendered permanently quaternary by the double bond. In such an ester we should not, in view of the above-mentioned generalisation, expect to find any tendency to acquire an atom of hydrogen, which,

if it were acquired, could not possibly be mobile. If, on the contrary, we found that an ester of the type IX actually did possess a noteworthy tendency to acquire a hydrogen atom in place of its carbethoxyl group, we should have to look on the fact as evidence of the tautomeric or dynamic character of the three-carbon system (1), (2), (3) of the indene ring. This follows by simply reversing the argument.

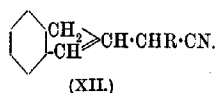
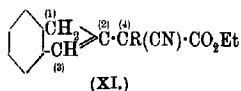
Actually, we have succeeded in preparing a number of indenyl 3-cyanoacetic esters of the type IX, and have found that the lower members of the series possess a very marked tendency to lose their carbethoxyl group as ethyl carbonate when treated with quite a small quantity of sodium ethoxide at 30°. The ester in which R=Me, for example, when treated with as little as one-sixth of a molecule of sodium ethoxide, reacts at 30° in the course of a few minutes. The yield of the decarbethoxylated nitrile is 60 per cent., the remainder of the material passing into an insoluble substance of high molecular weight. In all the cases of this reaction investigated, there was a greater or less quantity of insoluble by-product formed along with the nitrile X and ethyl carbonate.



With homologous alkyl derivatives (R=Et and R=Pr<sup>n</sup>), the reaction becomes successively more sluggish, and an increased quantity of by-product is formed, the yield of nitrile consequently diminishing. This is quite analogous to all that has been observed in regard to the same reaction when applied to the glutaconic esters (T., 1911, 99, 2192). Two points, to which no analogy has as yet been investigated or observed among the glutaconic esters, require, however, special notice. The ester for which R=allyl was found to be very much more reactive than the corresponding *n*-propyl derivative. Its reactivity was quite of a similar order to that of the methylated ester. The other point is that a branched chain in the alkyl group appears to inhibit the reaction practically altogether. Thus the esters for which R was *isopropyl*, *isobutyl*, and *isoamyl* gave no nitrile after remaining for twenty-four hours with one-sixth of a molecular proportion of sodium ethoxide at 30°.

In order to obtain a comparative check on these results, we decided to investigate an indenyl-2-cyanoacetic ester of the type XI. This clearly differs from IX only in the fact that in XI the

cyanoacetic residue is attached to the central carbon atom of the indene system. Now if the double bond in XI is entirely static as regards possible interchange across the system (1), (2), (3), then the carbon atom (4) will be the terminal carbon atom of one three-carbon system only, namely, the system (3), (2), (4).



It should therefore differ but little in reactivity from the carbon atom (4) in the corresponding ester of type IX. If, on the other hand, the system (1), (2), (3) of XI possesses a mobile hydrogen atom and a mobile double bond, it is clear that a hydrogen atom attached to the carbon atom (4) will have a double possibility of "wandering"; it might wander either to (1) or to (3). We might, therefore, in view of the general rule, expect to find an ester of the type XI even more prone than the corresponding ester of the type IX to exchange its carbethoxyl group for an atom of hydrogen.

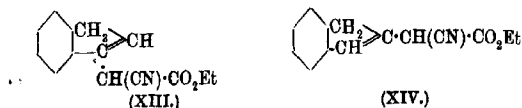
Experiment shows the latter supposition to be amply justified. The ester prepared was that for which  $R = \text{Me}$ . With one-twentieth molecular proportion of sodium ethoxide, there was obtained after three minutes at  $15^\circ$  a practically quantitative yield of the corresponding nitrile (XII:  $R = \text{Me}$ ).

This connexion between the ease of elimination of the carbethoxyl group and the potential mobility of the hydrogen attached to the carbon of the cyanoacetic residue suggests a possible explanation of the broad facts both in the indene and glutaconic series in regard to the effect of the size of an alkyl group on the ease of the reaction. It seems likely to be connected with the fact that when heavier alkyl groups were introduced into the glutaconic molecule, they were found to increase the stability of the unsaturated form, and consequently to reduce the predominance of the normal and the potential mobility of the tautomeric hydrogen atom (since tautomerism depends on the possibility of the existence of the normal form). An ester in which the degree of tautomerism of the three-carbon system has been so reduced by the entrance of a large alkyl group would, in view of the generalisation, be expected to exhibit a smaller tendency to acquire an atom of hydrogen, and this is what is actually found to be the case.

In complete accord with the great ease with which the ester XI exchanges its carbethoxyl group for an atom of hydrogen, and with the presumed excessive mobility of the latter, is the behaviour of the unmethyated ester XIV. The esters IX and XI were



obtained by alkylating the esters XIII and XIV respectively. These esters differ in acidity in the sense that, as one would expect from the different reactivities of their alkyl derivatives, the cyanoacetic hydrogen atom of indenyl-2-cyanoacetic ester (XIV) is more loosely attached than that of the corresponding indenyl-3-derivative (XIII). Thus ethyl indenyl-2-cyanoacetate is a weak acid

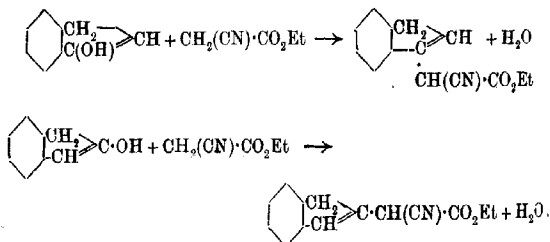


forming a sodium salt which is not hydrolysed in aqueous solution, being decomposed only by slightly acid substances, such as carbonic acid. Ethyl indenyl-3-cyanoacetate, on the other hand, only forms a sodium salt in complete absence of water.

It is perhaps worth noticing that when either of the indenylcyanoacetic esters (XIII and XIV) are converted into or liberated from their salts, a deep crimson colour is immediately developed. This fades in the course of a few seconds, both the free esters and the solid salts being colourless.

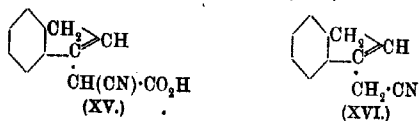
Another colour change which was regularly observed in the course of these experiments took place when the alkylated esters (IX and XI) were treated with sodium ethoxide. An indigo-blue colour immediately developed, and gradually faded as the elimination of the carbethoxyl group proceeded.

The preparation of the indenylcyanoacetic esters (XIII and XIV) was readily accomplished by condensing  $\alpha$ -hydrindone or  $\beta$ -hydrindone with ethyl cyanoacetate in the presence of piperidine or diethylamine:



When ethyl indenyl-3-cyanoacetate was hydrolysed either by acid or by alkali, the cyano-acid (XV) was formed, although not without considerable decomposition. This acid on heating above its melting point gave off carbon dioxide, and from the dark

coloured residue indenyl-3-acetonitrile (XVI) was isolated by



vacuum distillation. This is the first member of the series of homologous nitriles of which X is the type. It cannot, of course, be prepared directly from the cyano-ester (XIII) by the action of sodium ethoxide, for reasons already indicated.

Neither the compound, XVI, nor any of its homologues appears to form a sodium compound when treated with alcoholic sodium ethoxide, and all attempts to introduce another alkyl group into these compounds, using sodium or potassium ethoxide and an alkyl iodide, met with failure. The same was the case when the methylated nitrile, XII, derived from  $\beta$ -hydrindone, was used.

#### EXPERIMENTAL.

The  $\alpha$ -hydrindone required for these experiments was prepared from  $\beta$ -phenylpropionic acid by a method essentially the same as that described by Kipping (T., 1894, 65, 680), but with the introduction of certain modifications which so improved the yield as to make this substance far more easily available than it has hitherto been.

*$\beta$ -Phenylpropionyl Chloride.*—It was found advantageous to use thionyl chloride in the preparation of this substance instead of phosphorus pentachloride.  $\beta$ -Phenylpropionic acid (100 grams) was mixed with an equal weight of thionyl chloride in a flask fitted with an efficient condenser. The reaction was started by gentle heat and allowed to proceed for one and a-half to two hours, when the evolution of gas had ceased. The contents of the flask were then transferred to a Claisen distillation flask and heated at 100°/25 mm. until all the thionyl chloride had distilled over. The residue was then fractionated under 22·5 mm. pressure, and 110 grams boiling at 121—122° were collected. The theoretical yield is 112 grams.

*$\alpha$ -Hydrindone.*—Pure  $\beta$ -phenylpropionyl chloride being thus available, it was found possible to carry out the internal condensation, whereby hydrogen chloride is eliminated and  $\alpha$ -hydrindone produced, with much better results than Kipping was able to obtain with the impure chloride at his disposal. Whilst he seldom obtained more than a 56 per cent. yield, it was found that with the pure chloride a yield of 75 per cent. was always secured. The

reaction with the pure chloride is far more violent than with the impure product, and hence the mixture must be heated for a few minutes only. With this exception, the details given by Kipping were closely followed.

*$\beta$ -Hydrindone.*—The  $\beta$ -hydrindone required for these experiments was prepared by the improved modification (P., 1911, 27, 108) of the original process described by Moore and Thorpe (T., 1908, 93, 165).

*Condensation of  $\alpha$ -Hydrindone with Ethyl Cyanoacetate in the Presence of Secondary Bases: Ethyl Indenyl-3-cyanoacetate (XIII, p. 148).*

Since  $\alpha$ -hydrindone readily dissolves in ethyl cyanoacetate, it is not necessary to use any solvent in this condensation. A solution of 19 grams of the ketone in 16 grams of the ester was treated with 6.5 grams of diethylamine and the mixture allowed to remain at 40° for twenty-four hours. At the end of that time, the tube, which contained a stiff paste of crystals of the condensation product, was cooled for an hour at 0°, and the crystals were drained on porous porcelain. The compound separates from alcohol in colourless, needle-shaped crystals melting at 104°; it is moderately soluble in dry ether and readily so in benzene, chloroform, or acetone. The yield represents about 55 per cent. of the theoretical, and is but little affected when piperidine is used in place of diethylamine:

0.1031 gave 0.2805  $\text{CO}_2$  and 0.0538  $\text{H}_2\text{O}$ .  $\text{C}=74.20$ ;  $\text{H}=5.80$ .

0.2492 „ 13.8 c.c.  $\text{N}_2$  at 19° and 742.6 mm.  $\text{N}=6.19$ .

$\text{C}_{14}\text{H}_{18}\text{O}_2\text{N}$  requires  $\text{C}=74.0$ ;  $\text{H}=5.7$ ;  $\text{N}=6.2$  per cent.

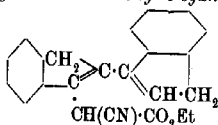
The ester reacts with alcoholic sodium ethoxide, forming a sodium compound, from which the ester is regenerated by the action of water. There is no doubt but that this sodium compound contains the metal attached to the cyanoacetic residue, and that therefore the ester described above has the constitution assigned to it. When alcoholic sodium ethoxide was added to the ester, a deep crimson colour was invariably formed. This faded after a few seconds to a bright yellow, which persisted so long as the solution remained alkaline.

*Condensation of  $\alpha$ -Hydrindone with Ethyl Cyanoacetate in the Presence of Alcoholic Sodium Ethoxide.*

The condensation with sodium ethoxide appears to be of a considerably more complex character than when secondary bases are used. Thus, when an alcoholic solution of  $\alpha$ -hydrindone is added

to a hot suspension in alcohol of the sodium compound of ethyl cyanoacetate, there is formed a mixture of substances which may be precipitated by adding water. This mixture consists chiefly of two compounds, melting at  $143^{\circ}$  and  $88-89^{\circ}$  respectively, which may be separated and obtained in a state of purity by fractional crystallisation, first from alcohol and finally from a mixture of absolute alcohol and benzene. The former compound was identified with anhydrobis- $\alpha$ -hydrindone (Found: C=87.74; H=5.70. Calc.: C=87.8; H=5.7 per cent.), which is recorded as melting at  $142-143^{\circ}$  (Kipping, T., 1894, 65, 495).

*Ethyl 2:3'-Di-indenyl-3-cyanoacetate,*



The substance melting at  $88-89^{\circ}$  may be made to become the principal product if the order in which the condensing substances are mixed is reversed. 3.3 Grams of  $\alpha$ -hydrindone were dissolved in a small quantity of hot alcohol, and a hot solution of 0.6 gram of sodium and 2.8 grams of ethyl cyanoacetate in 15 grams of alcohol was slowly added. A few minutes after the addition was complete, the solution was rapidly cooled and poured into water. Hydrochloric acid was then added, and the oily precipitate extracted with ether, the extract washed with dilute sodium carbonate solution and with water, and then dried. The solid residue obtained on evaporation of the ether, when recrystallised from alcohol, weighed 0.8 gram:

0.1545 gave 0.4575  $\text{CO}_2$  and 0.0790  $\text{H}_2\text{O}$ . C=80.78; H=5.68.

0.1818 „ 6.7 c.c.  $\text{N}_2$  at  $17^{\circ}$  and 766.1 mm. N=4.23.

$\text{C}_{23}\text{H}_{16}\text{O}_2\text{N}$  requires C=80.9; H=5.6; N=4.1 per cent.

*Ethyl 2:3'-di-indenyl-3-cyanoacetate* separates from the usual solvents in pinkish-buff needles melting at  $88-89^{\circ}$ . It is oxidised instantly by cold alkaline permanganate. With alcoholic sodium ethoxide, it forms a yellow sodium compound, from which the original ester can be regenerated.

*Hydrolysis of Ethyl Indenyl-3-cyanoacetate: Indenyl-3-cyanoacetic Acid (XV, p. 149).*

The hydrolysis of the ester melting at  $104^{\circ}$  is a matter of some difficulty, owing to the ease with which it undergoes deep-seated

decomposition with acids and alkalis. Thus, on boiling with acids (dilute hydrochloric or sulphuric), only a 6 per cent. yield of the acid is obtained. The acid can be produced in 36 per cent. yield by alkaline hydrolysis, but only by working within very narrow limits. Four grams of the ester were treated with 8 c.c. of 4*N*. sodium hydroxide, and the mixture was heated as rapidly as possible to the boiling point and maintained there for twenty seconds with vigorous shaking. The oil dissolved, forming a clear red solution, which was kept boiling for thirty seconds longer and then rapidly cooled. The crystalline sodium salt which separated was collected, dissolved in water, and the solution, after passing through a wet filter, acidified with hydrochloric acid. The acid separated as a white precipitate, which crystallised from alcohol in small prisms melting and decomposing at about 200°, the melting point depending on the rate of heating. The point of instantaneous decomposition as measured by the Maquenne block is 237°. The acid is sparingly soluble in water or dry ether:

0.1251 gave 0.3326 CO<sub>2</sub> and 0.0509 H<sub>2</sub>O. C=72.51; H=4.52.

0.2164 „ 13.8 c.c. N<sub>2</sub> at 19° and 755 mm. N=7.24.

C<sub>12</sub>H<sub>9</sub>O<sub>2</sub>N requires C=72.4; H=4.5; N=7.1 per cent.

*Indenyl-3-acetonitrile* (XVI, p. 149).

The pure, recrystallised acid (4.4 grams) was heated at 250° until the evolution of carbon dioxide had ceased. The dark-coloured oil which remained was then distilled under diminished pressure and the colourless distillate cooled in ice. The solid residue, which melted below the ordinary temperature, was recrystallised from light petroleum below 0°, and obtained in long, colourless needles melting at 18°:

0.0820 gave 0.2568 CO<sub>2</sub> and 0.0426 H<sub>2</sub>O. C=85.41; H=5.77.

0.1430 „ 11.3 c.c. N<sub>2</sub> at 19° and 761.2 mm. N=9.06.

C<sub>11</sub>H<sub>9</sub>N requires C=85.2; H=5.8; N=9.0 per cent.

The attempts which were made to alkylate this nitrile did not meet with any success, and we were quite unable to find the conditions by which the nitrile could be hydrolysed to the corresponding acid.

*Alkylation of Ethyl Indenyl-3-cyanoacetate and the Elimination of the Carboethoxyl Group: Ethyl α-Indenyl-3-α-cyano-propionate,*

$$\begin{array}{c} \text{CH}_2\text{CH} \\ | \\ \text{C}_6\text{H}_4 \end{array} \text{---} \text{C} \cdot \text{CMe}(\text{CN}) \cdot \text{CO}_2\text{Et}.$$

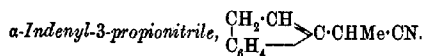
In order to prepare this substance, 12 grams of the ester melt-

ing at 104° were dissolved in the least possible quantity of alcohol at 70° and added to a solution of 1.2 grams of sodium in 16 grams of alcohol. Ten grams of methyl iodide were then added, and the mixture was heated until the yellow colour had entirely disappeared and the solution had become neutral, an operation which usually required ten minutes. The addition of water precipitated an oil which, when extracted by ether, yielded a solid residue after the solvent had been evaporated. The compound crystallises from a mixture of light petroleum and ether in large cubes melting at 60°; it is readily soluble in the usual organic solvents, excepting light petroleum. The yield was 70 per cent. of the theoretical:

0.1418 gave 0.3900 CO<sub>2</sub> and 0.0816 H<sub>2</sub>O. C=74.96; H=6.39.

0.2818 „ 14.4 c.c. N<sub>2</sub> at 19° and 783 mm. N=5.92.

C<sub>15</sub>H<sub>15</sub>O<sub>2</sub>N requires C=74.7; H=6.2; N=5.8 per cent.



Six grams of the carboxylic ester were dissolved in cold alcohol and an alcoholic solution containing 0.1 gram of sodium was added. The solution was kept at 30° for a short time, when the blue colour which had developed was discharged, and the liquid had a strong odour of ethyl carbonate. The liquid was poured through a filter, water was added, and the precipitate which was formed was induced to solidify by shaking. It was then collected, dried, and extracted with hot light petroleum, the nitrile being deposited from the solvent, on cooling, in long, colourless needles melting at 118°. It may also be recrystallised from dilute alcohol. The yield is 60 per cent. of the theoretical:

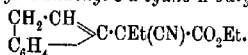
0.1032 gave 0.3227 CO<sub>2</sub> and 0.0603 H<sub>2</sub>O. C=85.28; H=6.49.

0.2118 „ 15.4 c.c. N<sub>2</sub> at 23° and 771 mm. N=8.30.

C<sub>12</sub>H<sub>11</sub>N requires C=85.2; H=6.5; N=8.3 per cent.

The nitrile could not be hydrolysed, and all attempts to introduce another alkyl group into it were without success.

*Ethyl α-Indenyl-3-α-cyano-n-butyrate,*

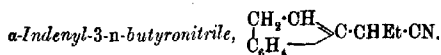


This ester was prepared in the same way as the methyl derivative already described. It is a colourless oil which boils at 200°/25 mm.:

0.1304 gave 0.3604 CO<sub>2</sub> and 0.0785 H<sub>2</sub>O. C=75.38; H=6.69.

0.2363 „ 11.6 c.c. N<sub>2</sub> at 22° and 768 mm. N=5.62.

C<sub>16</sub>H<sub>17</sub>O<sub>2</sub>N requires C=75.3; H=6.7; N=5.5 per cent.



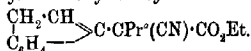
This nitrile was produced from the carboxylic ester by the action of a small quantity of alcoholic sodium ethoxide under the same conditions as those which were described for the methyl derivative. The crude solid precipitated by water was extracted with hot alcohol, and the nitrile obtained from the alcoholic extract by the addition of water. It crystallises from light petroleum in long needles melting at  $76^\circ$ . The yield is 20 per cent. of the theoretical:

0.1306 gave 0.4067  $\text{CO}_2$  and 0.0835  $\text{H}_2\text{O}$ .  $\text{C}=84.93$ ;  $\text{H}=7.11$ .

0.1882 „ 12.6 c.c.  $\text{N}_2$  at  $23^\circ$  and 771 mm.  $\text{N}=7.64$ .

$\text{C}_{13}\text{H}_{13}\text{N}$  requires  $\text{C}=85.2$ ;  $\text{H}=7.1$ ;  $\text{N}=7.7$  per cent.

*Ethyl  $\alpha$ -Indenyl-3- $\alpha$ -cyano- $n$ -valerate,*

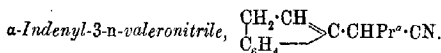


This ester was produced by the action of  $n$ -propyl iodide on the sodium compound of ethyl indenyl-3-cyanoacetate in alcoholic solution. The reaction was complete after heating for forty-five minutes, and the product was then isolated in the usual way. The ester is an oil which boils at  $210^\circ/20$  mm.:

0.1259 gave 0.3502  $\text{CO}_2$  and 0.0797  $\text{H}_2\text{O}$ .  $\text{C}=75.86$ ;  $\text{H}=7.03$ .

0.2169 „ 10.0 c.c.  $\text{N}_2$  at  $22^\circ$  and 768 mm.  $\text{N}=5.26$ .

$\text{C}_{17}\text{H}_{19}\text{O}_2\text{N}$  requires  $\text{C}=75.8$ ;  $\text{H}=7.1$ ;  $\text{N}=5.2$  per cent.



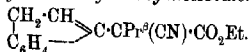
This compound was prepared in the same manner as the ethyl derivative, although in the present instance the reaction proceeded much less readily. It was isolated in the usual way and crystallised from light petroleum in colourless needles melting at  $67^\circ$ . The yield was only 10 per cent. of the theoretical:

0.1028 gave 0.3210  $\text{CO}_2$  and 0.0710  $\text{H}_2\text{O}$ .  $\text{C}=85.16$ ;  $\text{H}=7.68$ .

0.2018 „ 12.8 c.c.  $\text{N}_2$  at  $23^\circ$  and 768 mm.  $\text{N}=7.20$ .

$\text{C}_{14}\text{H}_{15}\text{N}$  requires  $\text{C}=85.3$ ;  $\text{H}=7.6$ ;  $\text{N}=7.1$  per cent.

*Ethyl  $\alpha$ -Indenyl-3- $\alpha$ -cyanoisovalerate,*



*iso*-Propyl iodide was found to react with the sodium compound

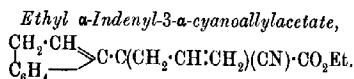
of ethyl indenyl-3-cyanoacetate in the same manner as *n*-propyl iodide, and the product was isolated in the same way. In this case, the ester was obtained as a colourless oil which boiled at 260°/120 mm., and solidified in the receiver. The solid crystallised from light petroleum in colourless prisms melting at 72°. The yield represented 60 per cent. of the theoretical:

0.1115 gave 0.3105 CO<sub>2</sub> and 0.0716 H<sub>2</sub>O. C=75.95; H=7.15.

0.1859 „ 8.6 c.c. N<sub>2</sub> at 22° and 768 mm. N=5.28.

C<sub>17</sub>H<sub>16</sub>O<sub>2</sub>N requires C=75.8; H=7.1; N=5.2 per cent.

This ester was scarcely changed by alcoholic sodium ethoxide under the experimental conditions which caused the other esters to lose their carbethoxyl groups as ethyl carbonate. Most of the original ester and a small amount of insoluble matter were recovered.

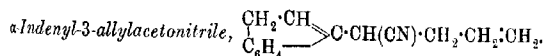


Allyl iodide reacted with the sodium compound of ethyl indenyl-3-cyanoacetate in boiling alcoholic solution in the course of a few seconds. The product was isolated in the usual way and crystallised from light petroleum containing a little dry ether in nearly cubical crystals melting at 65°. The yield was 65 per cent. of the theoretical:

0.1240 gave 0.3484 CO<sub>2</sub> and 0.0715 H<sub>2</sub>O. C=76.63; H=6.41.

0.2954 „ 13.6 c.c. N<sub>2</sub> at 19° and 764 mm. N=5.31.

C<sub>17</sub>H<sub>16</sub>O<sub>2</sub>N requires C=76.4; H=6.4; N=5.2 per cent.



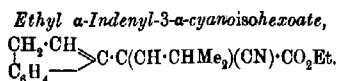
The action of a trace of alcoholic sodium ethoxide on the ester caused the carbethoxyl group to be eliminated, and gave a yield of 40 per cent. of the corresponding nitrile, the same conditions being employed as those described in the former experiments. The nitrile crystallises from light petroleum in colourless needles melting at 108°:

0.1064 gave 0.3366 CO<sub>2</sub> and 0.0647 H<sub>2</sub>O. C=86.28; H=6.75.

0.2732 „ 17.6 c.c. N<sub>2</sub> at 23° and 768 mm. N=7.31.

C<sub>14</sub>H<sub>13</sub>N requires C=86.2; H=6.7; N=7.1 per cent.





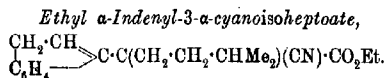
This ester was prepared in the usual manner from *isobutyl* iodide and ethyl indenyl-3-cyanoacetate. It distilled at 260°/40 mm. as a pale yellow oil:

0.1956 gave 0.5481 CO<sub>2</sub> and 0.1290 H<sub>2</sub>O. C=76.43; H=7.33.

0.2600 „ 11.6 c.c. N<sub>2</sub> at 22° and 761 mm. N=5.07.

C<sub>18</sub>H<sub>21</sub>O<sub>2</sub>N requires C=76.3; H=7.4; N=4.9 per cent.

Like the *isopropyl* derivative, this ester did not lose its carbethoxyl group by treatment with cold sodium ethoxide. After being submitted to the same experimental conditions as the other esters, the recovered material gave, on analysis, C=76.89, H=7.56, N=5.13, indicating that it was practically unchanged. (The de-carbethoxylated compound, C<sub>15</sub>H<sub>17</sub>N, requires C=85.3; H=8.1; N=6.6 per cent.)



When prepared from the ester melting at 104°, and *isoamyl* iodide, and isolated in the usual way, this ester distilled at 270°/34 mm. as an almost colourless oil:

0.1680 gave 0.4749 CO<sub>2</sub> and 0.1173 H<sub>2</sub>O. C=77.08; H=7.76.

0.2127 „ 9.0 c.c. N<sub>2</sub> at 22° and 766 mm. N=4.80.

C<sub>19</sub>H<sub>23</sub>O<sub>2</sub>N requires C=76.8; H=7.7; N=4.7 per cent.

The carbethoxyl group could not be eliminated under the customary experimental conditions. The material recovered from the solution of sodium ethoxide gave, on analysis, C=77.31, H=7.92, N=4.95, indicating that it consisted of the unchanged compound (C<sub>16</sub>H<sub>19</sub>N, the carbethoxyl-free compound, requires C=85.3, H=8.5, N=6.2 per cent.).

*Condensation of β-hydrindone with Ethyl Cyanoacetate in the Presence of Secondary Bases.*

When a mixture of β-hydrindone and ethyl cyanoacetate is treated with a secondary base such as piperidine or diethylamine, there is generally formed a mixture of two crystalline compounds melting at 116° and 176° respectively. The latter contained no nitrogen and gave, on analysis, C=87.62, H=5.81 (C<sub>18</sub>H<sub>14</sub>O requires C=87.8; H=5.7 per cent.). It is therefore probably

identical with anhydrobis- $\beta$ -hydrindone, the melting point of which is given as approximately  $170^{\circ}$  (Heusler and Schieffer, *Ber.*, 1899, 32, 32). The amount of bis-compound formed varies very much with the conditions, and unless the condensation is kept well under control it may become the sole product.

*Ethyl Indenyl-2-cyanoacetate* (XIV, p. 148).

By exercising care, it was found possible to obtain a solid product containing as much as 65 per cent. of ethyl indenyl-2-cyanoacetate and 35 per cent. of anhydrobis- $\beta$ -hydrindone. Ten grams of  $\beta$ -hydrindone were dissolved in 9 grams of ethyl cyanoacetate, and the solution was cooled below  $18^{\circ}$  while 30 drops of diethylamine were added. After the addition of each drop, the solution was immediately shaken and well cooled in running water. After completing the addition of the base, the tube containing the mixture was immersed in cold water for thirty minutes, when it was withdrawn and allowed to remain at the ordinary temperature for forty-eight hours. At the end of that time the stiff paste of crystals which filled the tube was spread on porous porcelain and allowed to remain until colourless. The crude solid mixture of condensation products, which usually weighed about 13 grams, was rubbed to a fine powder under a little dry ether and roughly separated by extracting with four times its weight of boiling 95 per cent. alcohol, the bulk of the bis-compound being left undissolved. The crude ester deposited by the filtrate melted between  $90^{\circ}$  and  $110^{\circ}$ . It was finely powdered and stirred into an excess of 4*N*-sodium hydroxide at  $30^{\circ}$ , the whole diluted with an equal bulk of water, quickly filtered, and treated with aqueous sodium hydrogen carbonate in excess. The precipitated ester was caused to solidify by shaking, and then collected and triturated with water. After draining and recrystallising from alcohol, it was obtained in long, colourless needles melting at  $116^{\circ}$ :

0.1261 gave 0.3417  $\text{CO}_2$  and 0.0646  $\text{H}_2\text{O}$ .  $\text{C} = 73.91$ ;  $\text{H} = 5.70$ .

0.1834 „ 9.7 c.c.  $\text{N}_2$  at  $16^{\circ}$  and 772.5 mm.  $\text{N} = 6.25$ .

$\text{C}_{14}\text{H}_{18}\text{O}_2\text{N}$  requires  $\text{C} = 74.0$ ;  $\text{H} = 5.7$ ;  $\text{N} = 6.2$  per cent.

The compound is very readily soluble in hot alcohol, but sparingly so in cold. It is also very readily soluble in cold benzene, chloroform, or acetone, and sparingly so in ether or light petroleum. It tends to form coloured products when its alkaline solution is exposed to the air, and the yield obtained by the sodium hydroxide separation therefore depends greatly on the speed with which the operations are carried out.

The separation was also effected by means of a long series of fractional distillations.

tional crystallisations from alcohol. The ester obtained by both methods proved to be the same substance, showing that the formation of a sodium salt had not involved any isomeric change, and that the compound must therefore have the structure assigned to it.

The ester is readily soluble in 4*N*-sodium hydroxide, and is not reprecipitated when a large bulk of water is added. It is insoluble, however, in sodium carbonate, and is therefore precipitated from the hydroxide solution by carbon dioxide or a bicarbonate. During the precipitation by either of these reagents or by an acid, a transient, red colour always appeared. A similar transient colour was invariably observed when an alcoholic solution of the ester was treated with aqueous or alcoholic potassium hydroxide or alcoholic sodium ethoxide.

*Sodium Derivative.*—One gram of the ester was dissolved in twice the theoretical quantity of 4*N*-sodium hydroxide at 50°. On cooling, a colourless, crystalline sodium derivative separated out. The alkaline liquid was poured off from the crystals, which were then washed with ice-water and dried in a vacuum over phosphoric oxide:

0.3002 gave 0.0860  $\text{Na}_2\text{SO}_4$ .  $\text{Na} = 9.28$ .

$\text{C}_{14}\text{H}_{12}\text{O}_2\text{NNa}$  requires  $\text{Na} = 9.24$  per cent.

When kept in a closed space, the sodium compound slowly decomposes, acquiring a green colour, but if spread in a thin layer over a large area in a dry atmosphere it can be kept for several weeks. Although the compound itself is colourless, its solution in water is orange. This solution on acidification becomes deep red for a few moments, the colour quickly fading as the free ester separates out.

*Methylation of Ethyl Indenyl-2-cyanoacetate and the Elimination of the Carbethoxyl Group: Ethyl  $\alpha$ -Indenyl-2- $\alpha$ -cyano-propionate,  $\text{C}_8\text{H}_4 \begin{smallmatrix} \text{CH}_2 \\ \text{CH} \end{smallmatrix} \gg \text{C} \cdot \text{Me}(\text{CN}) \cdot \text{CO}_2\text{Et}$ .*

The methylation of ethyl indenyl-2-cyanoacetate was accomplished both by the action of methyl iodide on the dry sodium compound suspended in alcohol and by the more usual process of treating the free ester with alcoholic sodium ethoxide and methyl iodide. The ester was precipitated with water and extracted with ether. After washing the extract with water and drying, the ether was evaporated and the residual oil crystallised from light petroleum containing a trace of ether. The ester separated in dense, colourless prisms melting at 56°. The yield was about 70 per cent. of the theoretical:

PREPARATION OF MONOMETHYLAMINE FROM CHLOROPICRIN. 159

0.1035 gave 0.2837 CO<sub>2</sub> and 0.0580 H<sub>2</sub>O. C=74.23; H=6.22.

0.1653 „ 8.4 c.c. N<sub>2</sub> at 18° and 779 mm. N=5.90.

C<sub>15</sub>H<sub>15</sub>O<sub>2</sub>N requires C=74.7; H=6.2; N=5.8 per cent.

*α*-Indenyl-2-propionate, C<sub>6</sub>H<sub>4</sub> $\begin{matrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH} \end{matrix}$ C·CHMe·CN.

The elimination of the carbethoxyl group of ethyl indenyl-2-cyanopropionate was found to proceed with great ease in the presence of a small quantity of sodium ethoxide. Thus with one-twentieth of a molecular proportion of sodium at 15°, the reaction was complete in about three minutes. On adding water, the nitrile separated out. After allowing the suspension to remain for twenty-four hours, it was filtered, and the solid dried and recrystallised from light petroleum, from which it separated in long, colourless needles melting at 92°:

0.1011 gave 0.3167 CO<sub>2</sub> and 0.0591 H<sub>2</sub>O. C=85.43; H=6.49.

0.1179 „ 8.5 c.c. N<sub>2</sub> at 20° and 764 mm. N=8.22.

C<sub>12</sub>H<sub>11</sub>N requires C=85.2; H=6.5; N=8.3 per cent.

The yield was practically quantitative.

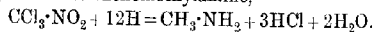
All attempts to hydrolyse this nitrile resulted in deep-seated decompositions taking place, and we were unable to isolate the corresponding acid. Several attempts also were made to introduce another methyl group into the molecule, but without success.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,  
SOUTH KENSINGTON, [Received, December 6th, 1918.]

XVII.—*The Preparation of Monomethylamine from Chloropicrin.*

By PERCY FARADAY FRANKLAND, FREDERICK CHALLENGER, and  
NOEL ALBERT NICHOLLS.

The products of the reduction of chloropicrin seem to vary with the nature of the reducing agent. With stannous chloride and hydrochloric acid, cyanogen chloride is produced (Raschig, *Ber.*, 1885, 18, 3326). The occasional formation of traces of ammonia was noticed by this chemist, but as a rule, after removing the tin by means of hydrogen sulphide, the product was found to be free from ammonium chloride and the hydrochlorides of hydroxylamine and methylamine. Iron filings and acetic acid (Geisse, *Annalen*, 1859, 109, 282) or tin and hydrochloric acid (Wallach, *ibid.*, 1877, 184, 51) give rise to monomethylamine,



Since chloropicrin may easily be obtained in large quantities, it appeared desirable more closely to investigate its reduction, owing to the importance of monomethylamine in synthetic organic chemistry. It would be inferred from Geisse's paper that the base he obtained was free from ammonia, whilst Wallach states that his product was comparatively very pure and the yield good.

By employing fine iron filings and hydrochloric acid, we have found that the composition of the reduction product depends on the conditions of the experiment. The use of iron and hydrochloric acid in the theoretical quantities (six atomic proportions of iron and nine molecular proportions of acid to one of chloropicrin) in such a way as to prevent the formation of ferrous or ferric hydroxides gave a product rich in ammonium chloride. If chloropicrin is shaken with iron filings and water, the mixture becomes extremely hot and a vigorous reaction sets in, which, however, gradually slackens if no acid is added. By adopting the method employed in the reduction of aromatic nitro-compounds or of nitromethane and nitroethane (Krause, *Chem. Zeit.*, 1916, **40**, 810), the reaction proceeds satisfactorily in the presence of only about one-fortieth of the theoretical amount of hydrochloric acid, and a practically theoretical yield of methylamine hydrochloride is obtained. This usually contains about 4 per cent. of ammonium chloride, but in some of our experiments the quantity of this impurity has been still further reduced. The best results have been obtained by slowly adding the chloropicrin to a well-stirred mixture of iron filings and acidified water. The gradual addition of iron filings to a mixture of acidified water and chloropicrin did not seem to be very satisfactory, so far as could be seen from the few experiments made in this direction. Some reductions carried out by gradually adding chloropicrin to boiling alkaline ferrous hydroxide failed to confirm the results of Geisse (*loc. cit.*), who states that by this method no ammonia is produced. We obtained a product containing about 20 per cent. of ammonium chloride.

The details of a typical large-scale experiment may be briefly outlined. Five hundred grams of fine iron filings were gradually shaken into a large earthenware jar containing 2500 c.c. of water and 60 c.c. of concentrated hydrochloric acid. In this way, the filings were thoroughly moistened and the tendency to clogging was diminished. The jar was fitted with a stirrer and placed in a little cold water; 250 grams of chloropicrin were then gradually added in the course of one-and-a-quarter hours. Too rapid addition of the chloropicrin caused the mixture to froth over. Owing to the large amount of hydrated oxide of iron produced, the stirring was as efficient as possible, otherwise chloropicrin escaped reaction through being enclosed in masses of iron filings or oxide.

The temperature rose considerably, and was maintained at about  $50^{\circ}$ , when the odour of chloropicrin was found to have disappeared after about three hours. The mixture was then gradually added to a boiling solution of sodium hydroxide contained in a large iron can, into which steam was blown. The methylamine was absorbed in hydrochloric acid, the solution evaporated, and the residue dried at  $110^{\circ}$  until constant weight was attained. The crude, dry hydrochloride was obtained in this way in a yield of 95.5 per cent., and contained 53.1 per cent. of chlorine, corresponding with an ammonium chloride content of only 3.5 per cent.

That ammonium chloride is actually produced during the reduction of chloropicrin was shown by treating cold concentrated aqueous solutions of the crude hydrochlorides with gaseous hydrogen chloride. The precipitated solid was collected, carefully freed from adhering hydrochloric acid, and analysed, when it was found to be almost pure ammonium chloride. The analyses of the crude methylamine hydrochloride were checked in some instances by an estimation of the platinum in the platinichloride. The hydrochlorides were evaporated with an excess of chloroplatinic acid solution, and the dry residue was extracted with absolute alcohol, whereby only platinum tetrachloride is removed. The possibility of a partial separation of the platinichlorides of the two bases would thus appear to be excluded.

#### Summary of Results.

*Section A.*—In the following experiments, the quantity of acid was very small, and the amount of iron theoretically required for the liberation of 12 atomic proportions of hydrogen (supposing sufficient acid had been present) was employed. The temperature was usually allowed to rise to about  $50$ – $70^{\circ}$ .

Experiment.	1.	2.	3.	4.	5.	6.
Chloropicrin, grams	500	250	250	25	25	25
Iron, grams	1000	500	500	50	50	50
Water, c.c.	3500	2500	2500	200	200	200
Hydrochloric acid, c.c.	100	60	60	12	32	10
Crude hydrochloride, grams	190	98	94	9.5	10.0	9.5
Theoretical weight, grams	205	102.5	102.5	10.2	10.2	10.2
Cl in crude hydrochloride	53.3	53.1	53.6	52.9	52.8	53.1
Hence percentage $\text{NH}_4\text{Cl}$	5.0	3.5	7.0	2.0	1.5	3.5
Pt in crude platinichloride	41.53	41.43	—	—	—	41.33
Hence percentage $\text{NH}_4\text{Cl}$	6.5	2.75	—	—	—	1.10

$\text{NH}_4\text{Cl}$  requires Cl = 66.5.  $(\text{NH}_4)_2\text{PtCl}_6$  requires Pt = 43.96.

$\text{CH}_3\text{NH}_2\text{Cl}$  requires Cl = 52.6.  $(\text{CH}_3\text{NH}_2)_2\text{PtCl}_6$  requires Pt = 41.36 per cent.

## 162 PREPARATION OF MONOMETHYLAMINE FROM CHLOROPICRIN.

*Section B.*—In the experiments described in this section, the quantity of acid employed was much larger (up to 9 molecular proportions, not including the three formed during the reduction), and the iron as in A. The chloropicrin and the acid were both added gradually to the iron filings. The percentage of ammonium chloride is seen to have increased considerably.

Experiment.	1.	2.	3.
Chloropicrin, grams.....	25	25	50
Iron, grams .....	50	50	100
Water, c.c. ....	100	50	100
Hydrochloric acid, c.c. ....	200	150	300
Yield of dry hydrochloride, grams .....	9	6.5	15.0
Theoretical weight, grams .....	10.2	10.2	20.5
Cl in crude hydrochloride .....	58.0	60.9	60.5
Hence percentage $\text{NH}_4\text{Cl}$ .....	40.0	60.0	60.0

*Section C.*—In these experiments, the chloropicrin was gradually added to a boiling alkaline ferrous sulphate solution. A considerable amount of ammonia was formed.

*Experiment I.*—Chloropicrin, 25 grams; ferrous sulphate, 550 grams; sodium hydroxide, 300 grams; water, 1800 c.c.

Dry hydrochloride, 7 grams. Theory, 10.2.

Analysis in samples of about 0.2 and 0.1 gram: Cl=56.0, 55.2. Mean=55.6, whence  $\text{NH}_4\text{Cl}$ =22 per cent.

*Experiment II.*—Quantities as in above.

Dry hydrochloride, 9 grams.

Analyses in samples of about 0.5 gram: Cl=54.8, 54.8, 54.6. Mean=54.7, whence  $\text{NH}_4\text{Cl}$ =15 per cent.

### *Interaction of Methylamine and 1:2:4-Trinitrobenzene.*

With 1:2:4-trinitrobenzene, the alcoholic solution of the base gave an almost immediate deposit consisting of yellow needles melting at 175—176°, and at 176° after one crystallisation. The formation of 2:4-dinitromethylaniline (m. p. 176—177°) by this method does not seem to have been described.

THE UNIVERSITY,  
BIRMINGHAM.

[Received, January 20th, 1919.]

# XVIII.—The Alkaloids of *Holarrhena congolensis*, Staff.

By FRANK LEE PYMAN.

FRÈRE JUST. GILLET, S.J., a missionary in the Belgian Congo, reported some years ago that, on chewing the leaves of *Holarrhena congolensis*, Staff, a local anæsthetic effect was produced on the mucous membrane of the mouth. This led the author to examine the alkaloids of the plant in 1913, when a new base, termed *holarrhenine*,  $C_{24}H_{38}ON_2$ , was isolated, together with the alkaloid *conessine*, which has been obtained previously by several authors from other species of *Holarrhena*. The physiological action of *conessine* and *holarrhenine* was studied by J. H. Burn (*J. Pharmacol.*, 1915, **6**, 305), who found that whilst they had a local anæsthetic action, this property was of no practical value, since they produced local necrosis when injected subcutaneously.

Since it is improbable that the author will continue this investigation, it is desired to put on record the properties of *holarrhenine* and also the results of a few experiments on *conessine* carried out at that time. These are for the most part in agreement with the recent work of Giemsa and Halberkann (*Arch. Pharm.*, 1918, **256**, 201), and confirm the formula  $C_{24}H_{40}N_2$  supported by these authors, not that  $C_{23}H_{38}N_2$ —put forward by Ulrici (*Arch. Pharm.*, 1918, **256**, 57). Giemsa and Halberkann's view, that *conessine* contains two dialkylamino-groups, is not shared by the present author, who found *conessine* to contain only three alkyl groups (no doubt methyl groups) attached to the nitrogen atom. Moreover, Polstorff and Schirmer (*Ber.*, 1886, **19**, 84) showed that *conessine* dimethoxide yields, on heating, a crystalline base, together with "ammonia" (doubtless trimethylamine). It is therefore probable that *conessine* contains an *N*-methyl group forming a link in a heterocyclic ring, to which a side-chain bearing a dimethylamino-group is attached. *Holarrhenine* resembles *conessine* in containing three *N*-alkyl groups. It yields a *monoacetyl* derivative,  $C_{26}H_{40}O_2N_2$ , which is diacidic, whence it follows that *holarrhenine* contains a hydroxyl group.

## EXPERIMENTAL.

### Isolation of the Alkaloids.

Twenty-nine kilograms of the bark of the trunk of *Holarrhena congolensis*, Staff, were percolated with very dilute hydrochloric



acid. The liquor was made alkaline with ammonia and extracted with chloroform. After distillation of the solvent, the dark, viscous residue was extracted first with light petroleum and then with ether. The light petroleum extract was shaken with dilute hydrochloric acid, the base regenerated with sodium carbonate, and extracted with light petroleum. The extract was distilled, and the residue dissolved in a solution of 0.7 part of hydrated oxalic acid in 4 parts (by weight) of alcohol. On keeping, a colourless, crystalline hydrogen oxalate (m. p.  $249^{\circ}$ ) separated in a yield amounting to 0.9 per cent. of the bark. The oxalate was dissolved in water, the base regenerated by sodium carbonate, and extracted with light petroleum. After distilling the extract, the residue was dissolved in a little acetone and kept, when conessine separated in colourless plates, amounting to 0.25 per cent. of the bark. A further quantity was obtained by working up the mother liquor.

The ethereal extract of the total alkaloids was extracted with dilute hydrochloric acid, and this was basified with ammonia and extracted first with light petroleum and then with ether. The light petroleum extract was worked up as before for conessine. The ethereal extract was concentrated and left for some time, when a small quantity of holarrhenine crystallised out.

#### *Conessine.*

The base employed in this investigation was purified by crystallisation from acetone, which is particularly suitable for the purpose, as Giemsa and Halberkann have remarked. The base is only sparingly soluble in cold acetone, but dissolves in boiling acetone to the extent of approximately 10 per cent. On cooling, it separates in large, colourless plates, which apparently contain acetone of crystallisation, for they effloresce quickly in the air, becoming free from solvent. The base melted at  $125^{\circ}$  (corr.).

Found: C=81.0, 80.7; H=11.3, 11.4; N=7.9; Me(attached to N)=12.5, 13.0.

$C_{24}H_{40}N_2$  requires C=80.8; H=11.3; N=7.9; Me(attached to N)=12.6 per cent.

The molecular weight was determined by the cryoscopic method in benzene:

0.2330 in 29.92 benzene gave  $\Delta t = -0.108^{\circ}$ . M.W.=361.

0.4442 „ 29.92 „ „ „  $\Delta t = -0.213^{\circ}$ . M.W.=349.

$C_{24}H_{40}N_2$  requires M.W.=356.5.

The specific rotatory power of the base was determined in chloroform solution:

$\alpha_D - 0.28^{\circ}$ ;  $c = 7.268$ ;  $l = 2$  dcm.;  $[\alpha]_D - 1.90^{\circ}$ .

The specific rotatory power of a specimen of the hydrobromide (containing 2·4 per cent. of water) was determined in aqueous solution:

$\alpha_D + 0.56^\circ$ ;  $c = 3.858$ ;  $l = 2$  dm.;  $[\alpha]_D + 7.4^\circ$  for the anhydrous salt.

*Conessine hydrogen oxalate* forms prisms readily soluble in hot, but rather sparingly so in cold, water, and sparingly soluble in alcohol. It melts and decomposes at  $280^\circ$  (corr.), and is anhydrous.

Found: C = 62.5; H = 8.1.

$C_{24}H_{40}N_2 \cdot 2C_2H_2O_4$  (536.5) requires C = 62.6; H = 8.3 per cent.

*Holarrhenine*,  $C_{24}H_{38}ON_2$ .

The crude base was first purified by crystallisation from ethyl acetate, when it melted at  $190^\circ$ , and then converted into the hydrobromide. This salt was crystallised from water and washed with acetone. It was then reconverted into the base, and this was recrystallised from ethyl acetate, when it separated in silky needles which melted at  $197-198^\circ$  (corr.). It suffers no loss at  $100^\circ$ . It is insoluble in water, readily soluble in alcohol or chloroform, but sparingly so in cold ethyl acetate, acetone, or ether.

Found: C = 77.5, 77.6, 77.3; H = 10.2, 10.3, 10.7; N = 7.7;

Me(attached to N) = 11.1, 12.2.

$C_{24}H_{38}ON_2$  (370.4) requires C = 77.8; H = 10.3; N = 7.6;

Me(attached to N) = 12.2 per cent.

The specific rotatory power was determined in chloroform solution:

$\alpha_D - 0.75^\circ$ ;  $c = 5.248$ ;  $l = 2$  dm.;  $[\alpha]_D - 7.1^\circ$ .

The *hydrobromide* crystallises from water in flat needles, which melt at  $265-268^\circ$  (corr.) after drying. It is readily soluble in hot, somewhat sparingly so in cold, water. The air-dried salt contains  $3H_2O$  (Found:  $H_2O = 9.0$ . Calc.:  $H_2O = 9.2$  per cent.).

Found, in salt dried at  $100^\circ$ , C = 54.4; H = 8.2; Br = 29.8.

$C_{24}H_{38}ON_2 \cdot 2HBr$  (532.3) requires C = 54.1; H = 7.6; Br = 30.0 per cent.

The specific rotatory power was determined in aqueous solution:  $\alpha_D + 1.02^\circ$ ;  $c = 4.630$ ;  $l = 2$  dm.;  $[\alpha]_D + 11.0^\circ$  or  $+12.1^\circ$  for the anhydrous salt.

*Acetylholarrhenine*, prepared by the action of acetic anhydride and anhydrous sodium acetate on holarrhenine, crystallises from acetone in large, colourless, oblong plates which melt at  $180^\circ$  (corr.).

166 PYMAN: ALKALOIDS OF HOLARRHENA CONGOLENSIS. STAFF.

It is insoluble in water, sparingly soluble in cold alcohol, acetone, or ether, but readily so in chloroform.

Found: C=75.7; H=9.9; N=6.8.

Equivalent to HCl, using methyl-orange=202.

$C_{28}H_{40}O_2N_2$  (412.5) requires C=75.7; H=9.8; N=6.8 per cent.

THE WELLCOME CHEMICAL WORKS.

DARTFORD, KENT,

[Received, February 4th, 1919.]

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## Organic Chemistry.

**Methane.** WILLIAM MALISOFF and GUSTAV EGLOFF (*J. Physical Chem.*, 1918, **22**, 529—575).—A summary is given of the work which has been published, from all sources, on the physical and chemical properties of methane, and a number of important problems requiring investigation are enumerated. [See *J. Soc. Chem. Ind.*, 1919, 35A.] E. H. R.

**Organic Chemical Reagents. II. Amylene.** *tert*-Amyl Alcohol. ROGER ADAMS, O. KAMM, and C. S. MARVEL (*J. Amer. Chem. Soc.*, 1918, **40**, 1950—1955).—Dehydration of primary alcohols by sulphuric acid generally proceeds less satisfactorily as the molecular weight of the alcohol increases. Amylene may, however, be satisfactorily obtained from commercial amyl alcohol under the following conditions. Amyl alcohol (1.5 litres) and concentrated sulphuric acid (100 c.c.) are heated to vigorous boiling under a reflux condenser in which the water is maintained at such a temperature (60—90°) as to allow a considerable amount of vapour to distil out of the apparatus; the top of the condenser is connected with a second, efficiently cooled condenser, attached so as to permit downward distillation. The heating requires a maximum time of about eight hours. At first, water and amyl alcohol pass over, whilst subsequently amylene distils. The distillate is washed with sodium hydroxide to remove sulphur dioxide and the amylene isolated by fractionation. It appears to consist of  $\beta$ -methyl- $\Delta^2$ -butylene and  $\beta$ -methyl- $\Delta^3$ -butylene containing only a negligible amount of  $\gamma$ -methyl- $\Delta^2$ -butylene. The residue in the original flask contains amyl alcohol and *iso*amyl ether, which are recovered by distillation with steam and subsequent fractionation. About 250 c.c. of amylene, 400 c.c. of *iso*amyl ether, and 500 c.c. of amyl alcohol are obtained from 1500 c.c. of the latter.

Larger amounts of amylene are more conveniently obtained by the pyrogenic-catalytic method, using aluminium oxide as catalyst at 500—540°. A suitable electrically heated furnace is fully described. The general procedure is similar to that indicated by Ipatieff (*A.*, 1903, i, 593). The yield of amylene is 70—80% of the theoretical, and the product is about 98—99% pentene. The catalyst retains its activity over lengthy periods.

*tert*-Amyl alcohol is prepared by the gradual addition of amylene to a mixture of concentrated sulphuric acid and ice. The product is diluted with ice-water (after removal of any unchanged amylene), rendered alkaline with sodium hydroxide, and distilled. 275—300 Grams of a product, b. p. 100—103°, may be obtained from 325 grams of amylene. H. W.

**Geometrical Isomerism.** A. E. LACOMBLÉ (*Chem. Weekblad*, 1918, **15**, 605—610).—The inconsistencies which are introduced

by the attempts to explain the existence of the *cis*- and *trans*-isomerides of ethylenic compounds of the type  $(A,B)C=C(A,B)$  by the theories of Werner and Stark are pointed out. All such theories set out to explain how the existence of the double bond prevents free rotation of the two doubly-linked carbon atoms about the line joining their centres. The explanations of Werner and of Stark are shown to be inconsistent with the hypotheses which they put forward as to the nature of the atoms and the mechanism by which the atoms are linked together. The author points out that it is hopeless to attempt to base an hypothesis of the structure of the benzene ring, for example, on theories which are inadequate to explain the mechanism of the double bond.

S. I. L.

**Derivatives of Trihalogeno-*tert*.-butyl Alcohols. II. The Propionic and Butyric Esters of Tribromo-*tert*.-butyl Alcohol (Brometone).** T. B. ALDRICH (*J. Amer. Chem. Soc.*, 1918, **40**, 1948—1950. Compare Aldrich and Beckwith, A., 1917, i, 77).— $\beta$ -Tribromomethylpropan- $\beta$ -ol is converted into the corresponding *propionate*, white crystals, m. p.  $27^{\circ}$ , by the action of propionyl chloride. The similarly prepared *butyrate* is an oil, b. p.  $144$ — $145^{\circ}/13$ — $14$  mm. Both are comparatively inactive pharmacologically, due probably to their not being decomposed into soluble constituents having a typical physiological action and are rather slowly absorbed.

H. W.

**Glyceryl Methyl Ether Dinitrate ( $\alpha$ -Methylin Dinitrate).** DAVID TREVOR JONES (T., 1919, **115**, 76—81).

**The Action of Sodium Hydroxide on Carbon Monoxide, Sodium Formate, and Sodium Oxalate.** MAITLAND C. BOSWELL and J. V. DICKSON (*J. Amer. Chem. Soc.*, 1918, **40**, 1779—1786).—It has been shown (this vol., ii, 63) that fused sodium oxide is very active in effecting oxidations. It is now demonstrated that at  $410$ — $430^{\circ}$ , carbon monoxide in contact with fused sodium hydroxide is oxidised to carbon dioxide, an equivalent amount of hydrogen being produced at the same time. Sodium formate when fused with sodium hydroxide at  $275^{\circ}$ , a temperature much below its decomposition temperature, is oxidised almost quantitatively to carbon dioxide in a very short time, an equivalent amount of hydrogen also being formed. Sodium oxalate is similarly oxidised at  $290^{\circ}$ . In both these cases, it is the water present in the fusion, catalysed by the sodium hydroxide, which is the effective oxidising agent. It is held that the general reaction involving the replacement of the carboxyl group by hydrogen in alkali fusions, for example, in the formation of benzene from sodium benzoate, involves simultaneous oxidation and reduction by the oxygen and hydrogen of water. [See also *J. Soc. Chem. Ind.*, 1919, February.]

E. H. R.

**Quinonoid Character of Maleic Anhydride.** PAUL PREIFFER and THEODOR BÖTTLER (*Ber.*, 1918, **51**, 1819—1829. Compare Pratt and Perkins, A., 1918, i, 167).—Maleic anhydride is related

to furan in the same manner as quinone to benzene; it may therefore be regarded as a quinone of furan, and, in the present communication, evidence is adduced to show that the formal analogy is reproduced in its properties.

A characteristic property of quinones is their ability to yield more or deeply coloured molecular compounds with aromatic hydrocarbons, amines, phenols, and phenol ethers (A., 1914, i, 551; 1917, i, 205); this property is shared by maleic anhydride, which, although yielding colourless solutions in benzene, toluene, or *m*-xylene, gives coloured solutions with durene, hexamethylbenzene, naphthalene, 2:4:5:2':4':5'-hexamethylstilbene, *o*-tolyl methyl ether, and quinol and dimethylaniline. The influence of substituents in the molecule of the solute and solvent, respectively, is similar in the cases of *p*-benzoquinone and of maleic anhydride. Thus, methylation in the quinone molecule exerts a hypsochromic action on the colour of the quinhydrone; similarly, solutions of citraconic anhydride are less intensely coloured than corresponding solutions of maleic anhydride. Methylation in the benzenoid component produces a deepening of colour in the cases of *p*-benzoquinone and of maleic anhydride. The introduction of an *ortho*-condensed benzene nucleus has a similar influence in each instance, as is proved by the comparison of  $\alpha$ -naphthaquinone with *p*-benzoquinone on the one hand and of phthalic anhydride with maleic anhydride on the other. The deepening in colour caused by the introduction of halogen atoms into the quinone molecule is remarkably characteristic; the same effect is produced in the anhydrides, as proved by examination of bromomaleic, dibromomaleic, and tetrachlorophthalic anhydrides. Attempts to isolate the additive compounds of maleic anhydride or its bromo- or methyl derivatives in the crystalline state were not successful, but similar substances were readily obtained from tetrachlorophthalic anhydride and durene (long, pale yellow needles) and hexamethylstilbene (orange-coloured, shining leaflets, m. p. 183—184°), respectively.

The effect of alteration in the structure of the anhydride has also been investigated. Succinic anhydride yields colourless solutions in all the media mentioned above, whilst the solutions of itaconic anhydride are much less deeply coloured than those of citraconic anhydride. When dissolved in dimethylaniline, itaconic anhydride is gradually isomerised to citraconic anhydride. On passing from the anhydride to the corresponding acid or its esters, the quinonoid character is largely lost and the solutions are colourless or less intensely coloured, as is shown at the instances of maleic and dibromomaleic acids, of methyl fumarate, and of methyl tetrachlorophthalate. The substance,  $\text{CO}_2\text{H}\cdot\text{CBr}\cdot\text{CBr}\cdot\text{CHO}$ , scarcely possesses any quinonoid characteristics, but these are more marked with *trans*-dibenzoyl ethylene.  $\gamma$ -Pyrone and the ketones of the distyryl ketone series are less nearly related to quinone than is maleic anhydride; the former yields completely colourless solutions, whilst those of the latter only show faint colorations.

It was to be expected that imides of the type of maleinimide

would also show quinonoid characteristics; this is actually the case, but solutions of citraconanil and tetrachlorophthalimide are less deeply coloured than those of citraconic and tetrachlorophthalic anhydrides.

Maleic, citraconic, phthalic, and tetrachlorophthalic anhydrides do not exhibit halochromic phenomena when treated with concentrated sulphuric acid, trichloroacetic acid, or tin tetrabromide. Further investigation of this problem has led to the conclusion that the carbonyl groups of the substances which yield quinhydrone and of typical halochromic compounds must differ markedly in their chemical nature. H. W.

#### Oxidation of Organic Compounds by Silver Oxide.

ROBERT BEHREND and KARL DREYER (*Annalen*, 1918, 416, 203—225).—It has long been known that many acids and alcohols are oxidised by silver oxide, but hitherto a systematic investigation has not been made of the relation between the constitutions of substances and their tendency to oxidation or of the nature and quantity of the products of oxidation. The present paper deals with these points in the case of the simpler, hydroxylic aliphatic compounds. In order that a substance may be oxidised by silver oxide in alkali hydroxide or ammoniacal solution, it must contain a  $\text{:CH}\cdot\text{OH}$  (or  $\text{:CO}$  or  $\text{C[OH]}_2$ ) group combined with two  $\text{--CH}_2\cdot\text{OH}$ , two  $\text{:CH}\cdot\text{OH}$ , or two  $\text{--CO}_2\text{H}$  groups, or with any two of these three groups. Tartronic, tartaric, dihydroxytartaric, glyceric, mucic, saccharic, and gluconic acids, dextrose, glycerol, and mannitol are thus oxidised. For oxidation in neutral or acid solution, it suffices that the  $\text{:CH}\cdot\text{OH}$  group shall be combined with a carboxyl group and also with H,  $\text{CH}_2$ , or  $\text{CH}_3$ . Glycollic, lactic, malic (and also formic) acids are thus oxidised. Propylene glycol, ethyl alcohol, isopropyl alcohol, and oxalic acid suffer little or no oxidation. In alkali hydroxide solution, substances of the group first mentioned are oxidised rapidly and completely; the rate of oxidation is accelerated, but the relative quantities of the products of oxidation are unaffected by an increased concentration of the alkali hydroxide. In ammoniacal solution, silver oxide oxidises the alkali salts of the acids completely in fifty minutes at  $90^\circ$ . The acids are more easily oxidised in the form of alkali salts than in the form of ammonium salts. An excess of ammonia or of ammonium salt retards the oxidation.

The products of oxidation in alkaline solution contain at most two atoms of carbon, and are never obtained in simple molecular proportions. All the substances with the exception of glycerol yield carbon dioxide as one of the products of oxidation in acid or in alkaline solution. Formic acid is a product of oxidation in alkaline solution, and then only if the oxidisable substance contains a  $\text{:CH}\cdot\text{OH}$  group united with a  $\text{:CH}\cdot\text{OH}$  or  $\text{--CH}_2\cdot\text{OH}$  group as well as with a  $\text{:CH}\cdot\text{OH}$ ,  $\text{--CH}_2\cdot\text{OH}$ , or  $\text{--CO}_2\text{H}$  group. Formic acid may be an intermediate product of oxidation in acid solution, but in such circumstances it undergoes further oxidation. Oxalic

acid is almost always the chief product of oxidation in alkaline solution; in neutral or acid solution, it is formed in much smaller quantity. In neutral solution, malic acid yields malonic acid, and lactic acid and propylene glycol yield acetic acid. C. S.

**Tartronic Acid.** ROBERT BEHREND and AUGUST PRÜSSE (*Annalen*, 1918, **416**, 233—239).—Tartronic acid has been prepared by eleven investigators, who record eight different m. p.'s between 145° and 185°. The correct value appears to be 156—158° (decomp.). C. S.

**Preparation of Gulonolactone.** F. B. LA FORGE (*J. Biol. Chem.*, 1918, **36**, 347—349).—To a solution of 150 grams of xylose in 300 c.c. of water, 30 grams of hydrocyanic acid are added, and then a few drops of ammonium hydroxide. The reaction commences at once, and is completed in about six hours at 35°. Slightly more than one equivalent (55 grams) of sulphuric acid diluted with a small amount of water is added to the solution, which is then concentrated at once to a viscous syrup. Hydrolysis of the nitrile takes place, and on cooling and keeping, the lactone crystallises out. The yield after recrystallisation from 60% alcohol amounts to 55 to 60% of the weight of xylose used. H. W. B.

**Crystallography and Optical Properties of Three Aldopentoses.** EDGAR T. WHERRY (*J. Amer. Chem. Soc.*, 1918, **40**, 1852—1858).—The optical properties of the crystals of the three sugars  $\alpha$ -*D*-lyxose,  $\alpha$ -*D*-xylose, and  $\beta$ -*D*-arabinose enable them to be readily distinguished, and a determinative table is given for this purpose. For the determination of the refractive indices by the immersion method, suitable mixtures of turpentine oil ( $n$  1.47), clove oil ( $n$  1.53), and  $\alpha$ -bromonaphthalene ( $n$  1.66) are used.

$\alpha$ -*D*-Lyxose forms monoclinic, probably sphenoidal, crystals,  $a:b:c=1.608:1:1.828$ ;  $\beta=62^\circ 10'$ ; mean refractive index,  $n$  1.541;  $D^{20}$  1.545; molecular refraction,  $M$  30.60.

$\alpha$ -*D*-Xylose, rod-shaped, monoclinic, probably sphenoidal, crystals,  $a:b:c=1.655:1:1.776$ ;  $\beta=62^\circ 55'$ ;  $n$  1.536;  $D^{20}$  1.525;  $M$  30.67.

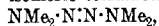
$\beta$ -*D*-Arabinose, rhombic, probably sphenoidal, needles,  $a:b:c=1.497:1:0.738$ ;  $n$  1.568;  $D^{20}$  1.605;  $M$  30.61.

Lyxose and xylose are obviously very closely related crystallographically, and  $\beta$ -arabinose, although crystallising in a different system from the others, shows closely similar inter-facial angles, and the three sugars form an essentially isomorphous group. The molecular refractivities are all slightly lower than that calculated from the atomic refractivities, 31.2. The divergence is probably due to some peculiarity of molecular configuration. E. H. R.

**Tetramethylammonium Azide.** FRANK V. FRIEDLANDER (*J. Amer. Chem. Soc.*, 1918, **40**, 1945—1947).—*Tetramethylammonium azide*,  $NMe_4N_3$ , is prepared by the gradual addition of a solution of tetramethylammonium iodide to an aqueous suspension of a slight excess of silver azide. The crystals belong to the tetragonal system ( $a:c=1.07245$ ). It is a fairly



stable substance which does not explode when struck with a hammer, when ground in a mortar, or when dropped on a hot plate; the dry salt begins to decompose at about 125°. Attempts to transform it into the isomeric tetramethyltetrazone,



have been unsuccessful up to the present.

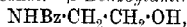
H. W.

**Glycosine.** ROBERT BEHREND and HERMANN KÖLLN (*Annalen*, 1918, **416**, 230—233).—In addition to glyoxaline, very small quantities of glycosine are obtained by the action of ammonia on glyoxal. The yield of glycosine is considerably increased by the following procedure. In a tall cylinder are placed 20 c.c. of nitric acid, D 1.4, containing ten to fifteen drops of fuming nitric acid, 25 c.c. of water, and 25 c.c. of paraldehyde, the three liquids being introduced with as little intermixture as possible. The cylinder is immersed in water, the level of which is higher than that of the liquids in the cylinder. When the liquids have intermixed after some days and the evolution of gas has ceased, the mixture is repeatedly evaporated with water to remove volatile acids as completely as possible, and the residual syrup is diluted to 50 c.c. with water, producing an approximately 20% solution of glyoxal. One-half of this solution is evaporated until the temperature is 120°, 25—30 grams of ammonium acetate which has been heated at this temperature are gradually added, the resulting brownish-black liquid is dried at 100—110° and treated with water. The black residue of crude glycosine is dried in air and then at 70°, dissolved in warm 35% hydrochloric acid (which is added drop by drop), the solution is diluted with water, boiled with animal charcoal (free from iron), filtered after keeping for twenty-four hours in the warm, the brown filtrate is boiled again with animal charcoal, and the colourless filtrate is neutralised by ammonia, whereby glycosine is obtained in 42.5% yield.

A modification of Pinner's method of preparing trichlorolactic acid from chloral is described.

C. S.

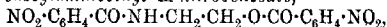
**$\beta$ -Aminoethyl Alcohol and its Derivatives.** SIGMUND FRÄNKEL and MARTHA CORNELIUS (*Ber.*, 1918, **51**, 1654—1662).—The following derivatives have been prepared to facilitate the identification of the amino-alcohol.  *$\beta$ -Benzoylaminoethyl alcohol*,



prepared by boiling an alcoholic solution of the dibenzoyl derivative with the quantity of solid potassium hydroxide calculated to eliminate one benzoyl group, forms colourless leaflets, m. p. 66—67°.  *$\beta$ -Acetylaminoethyl acetate*,  $\text{NHAc}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OAc}$ , b. p. 103°/0.049 mm., is obtained by boiling  $\beta$ -aminoethyl alcohol with acetic anhydride.  *$\beta$ -Acetylaminoethyl alcohol*, prepared from the amino-alcohol and acetyl chloride at 0°, forms colourless needles, m. p. 63—65°.  *$\beta$ -Naphthalenesulphonylaminoethyl alcohol*,  $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , asbestos-like crystals, m. p. 86—87°, is obtained by adding *N*-sodium hydroxide to an ethereal solution

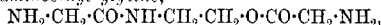
of  $\beta$ -naphthalenesulphonyl chloride (2 mols.) and  $\beta$ -aminoethyl alcohol (1 mol.), and subsequently acidifying the aqueous solution.

$\beta$ -m-Nitrobenzylaminoethyl m-nitrobenzoate,



colourless needles, m. p. 152—153°, obtained by heating  $\beta$ -aminoethyl alcohol (1 mol.) and m-nitrobenzoyl chloride on the water-bath, is reduced by the calculated quantity of tin and hydrochloric acid to  $\beta$ -m-aminobenzoylaminoethyl m-aminobenzoate hydrochloride,  $\text{C}_{16}\text{H}_{17}\text{O}_3\text{N}_3\cdot 2\text{HCl}$ , crystals, m. p. 232°.  $\beta$ -p-Nitrobenzoylaminoethyl p-nitrobenzoate, yellow needles, m. p. 188—189°, and  $\beta$ -p-aminobenzoylaminoethyl p-aminobenzoate, crystals, m. p. 206°, are obtained by similar methods.  $\beta$ -Phenylcarbamidoethyl phenylcarbamate,  $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{NHPh}$ , colourless crystals, m. p. 190—191°, is obtained by adding phenylcarbimide drop by drop to cold  $\beta$ -aminoethyl alcohol, and then heating the mixture in a sealed tube at 100°.  $\beta$ -Aminoethyl hydrogen sulphate,  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{SO}_3\text{H}$ , colourless crystals, m. p. 230°, is obtained from the amino-alcohol and fuming sulphuric acid in a freezing mixture.

$\beta$ -Glycylaminoethyl glycine,



obtained by adding chloroacetyl chloride (2 mols.) to a chloroform solution of  $\beta$ -aminoethyl alcohol (1 mol.) at 0° in the presence of lead carbonate, warming the mixture for a moment on the water-bath, and, after the cessation of the reaction and evaporation of the chloroform, treating the residual yellow syrup with concentrated aqueous ammonia, is a yellow syrup which is converted by the Schotten-Baumann method into  $\beta$ -hippurylaminoethyl hippurate,  $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NHBz}$ , colourless leaflets, m. p. 144°.

Dicarbamidoethyl carbonate,  $\text{CO}\left\langle\begin{array}{c} \text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O} \\ \text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O} \end{array}\right\rangle\text{CO}$ , crystals,

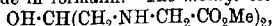
m. p. 88—90°, is obtained by the prolonged action of carbonyl chloride on  $\beta$ -aminoethyl alcohol in chloroform solution in the presence of lead carbonate.

$\beta$ -Aminoethyl alcohol in very dilute solution responds to the iodoform test. By treating an aqueous solution of the amino-alcohol with sodium nitrite and Ehrlich's reagent (2% alcoholic p-dimethylaminobenzaldehyde and dilute hydrochloric acid), an intense canary-yellow coloration is produced which is not destroyed by warming or by the addition of aqueous ammonia or potassium hydroxide.

$\beta$ -Benzoylaminoethyl alcohol,  $\beta$ -m-aminobenzoylaminoethyl m-aminobenzoate hydrochloride, and  $\beta$ -p-aminobenzoylaminoethyl p-aminobenzoate are not anaesthetics. C. S.

$\beta$ -Hydroxytrimethylenediglycine. HUGO KRAUSE (*Ber.*, 1918, 51, 1556—1571. Compare A., 1918, i, 156, 337).— $\beta$ -Hydroxytrimethylenediglycine has  $D_4^{25}$  1.348 by the swimming method. Its solution in formalin or water produces on a pine shaving a greenish-yellow, but not very intense, coloration; the reaction may

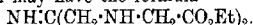
be used as a sensitive method of detecting glycine. The coloration is destroyed by alkali hydroxide or carbonate and by ammonia. Esters of  $\beta$ -hydroxytrimethylenediglycine are obtained by the action of aqueous sodium hydroxide on a solution of the glycine ester hydrochloride in formalin. The methyl ester,



a viscous, colourless liquid still containing 10% of formaldehyde,  $D^{15}_{\text{D}}$  1.18, is obtained in only 19% yield, but the ethyl ester is more readily obtained. When pure, it has b. p. 140—150°/16 mm. (partial decomp.),  $D^{15}_{\text{D}}$  1.150, and a molecular weight in benzene or naphthalene corresponding with its formula. It is comparatively stable towards sodium hydroxide, but is decomposed quantitatively by cold dilute hydrochloric acid, yielding methyl alcohol, formaldehyde, and ethyl glycine hydrochloride.

When the ethyl ester (84% purity) is heated at 16—18 mm., the distillate, apart from formaldehyde and unchanged ester, consists of a pale yellow oil, b. p. 200°/16 mm., which appears to be ethyl methyleneglycine,  $\text{CH}_2\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , or ethyl ethylenediglycine,  $\text{C}_2\text{H}_4(\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$ , more probably the former.

In the expectation of preparing the amide, ethyl  $\beta$ -hydroxytrimethylenediglycine was heated with alcoholic ammonia at 68—70° for twenty-four hours, but the chief product was a substance,  $\text{C}_{11}\text{H}_{21}\text{O}_4\text{N}_3$ , which may have the formula



The silver salt,  $\text{C}_9\text{H}_{15}\text{O}_3\text{N}_3\text{Ag}$ , previously described (*loc. cit.*), can also be prepared by dissolving glycine in 30% formaldehyde solution in the cold, neutralising this solution immediately with 4*N*-potassium hydroxide (phenolphthalein as indicator), and adding 20% silver nitrate solution. It is decomposed in aqueous suspension by hydrogen sulphide, yielding formaldehyde and glycine. The acid corresponding with the silver salt is therefore probably *N*-hydroxymethylglycine,  $\text{OH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ .

C. S.

#### Comparisons and Similarities: Water and Ammonia.

G. CIAMICIAN (*Atti R. Accad. Lincei*, 1918, [v], 27, ii, 141—146). —Attention is directed to the chemical analogy between  $\text{OH}_2$  and  $\text{NH}_3$ , between  $\cdot\text{OH}$  and  $\cdot\text{NH}_2$ , and between  $\cdot\text{O}$  and  $\cdot\text{NH}$  (compare Angeli, A., 1910, ii, 844, 948; 1915, i, 847). Such analogy is clearly shown in the relation between  $\text{C}\cdot\text{O}$  and  $\text{C}\cdot\text{NH}$ , the ready oxidation of cyanides to cyanates corresponding with that of carbon monoxide to carbon dioxide, and the reduction by zinc of cyanic acid with that of carbon dioxide. These relations are further rendered evident by the following series of equations:  $\text{CO}_2 + \text{H}_2\text{O} = \text{CO}(\text{OH})_2$ ;  $\text{CO}_2 + \text{NH}_3 = \text{OH}\cdot\text{CO}\cdot\text{NH}_2$ ;  $\text{O}\cdot\text{C}\cdot\text{NH} + \text{NH}_3 = \text{CO}(\text{NH})_2$ ;  $\text{C}(\cdot\text{NH})_2 + \text{H}_2\text{O} = \text{CO}(\text{NH})_2$ ;  $\text{C}(\cdot\text{NH})_2 + \text{ROH} = \text{OR}\cdot\text{C}(\cdot\text{NH})\cdot\text{NH}_2$ ;  $\text{C}(\cdot\text{NH})_2 + \text{NH}_3 = \text{NH}\cdot\text{C}(\text{NH}_2)_2$ . The polymerisation of cyanamide to dicyanodiamide corresponds with the synthesis of guanidine and its derivatives, the two tautomeric forms of cyanamide being regarded as reacting:  $\text{C}(\cdot\text{NH})_2 + \text{CN}\cdot\text{NH}_2 = \text{NH}_2\cdot\text{C}(\cdot\text{NH})\cdot\text{NH}\cdot\text{CN}$ . Other similar analogies are recorded.

T. H. P.

**Formation of Carbamide from Ammonium Carbonate and Related Substances.** FR. FICHTER, HEINRICH STRIGER, and THEOPHIL STANISCH (*Verh. Schwed. Nat. Ges.*, 1916, **28**, ii, 86—103; from *Chem. Zentr.*, 1918, ii, 444—446).—In a previous communication (Fichter, Stutz, and Grieshaber, A., 1913, i, 713), the formation of carbamide by the electrolysis of ammonium carbamate was attributed to the intermediate production of formamide by the action of hydroxylamine on ammonium carbamate; this view can no longer be maintained, since direct experiment shows that ammonium carbamate is not reduced by hydroxylamine. On the other hand, carbon dioxide reacts with hydroxylamine in the same manner as with ammonia, giving, according to conditions, hydroxylamine carbonate or the dihydroxylamine salt of hydroxycarbamic acid,  $\text{OH}\cdot\text{NH}\cdot\text{CO}_2\text{H}_2\text{N}\cdot\text{OH}$ . The experiments on the electrolysis of ammonium carbamate solution (*loc. cit.*) have therefore been repeated, the same solution being used as in previous experiments, but every care being taken to keep the anode and cathode solutions separate by enclosing the electrodes in porous pots immersed in a trough, all vessels containing the same solution. The results show that carbamide is produced exclusively at the anode, but no trace of a corresponding reduction product, such as formic acid or formamide, could be detected at the cathode. Under the experimental conditions, Liebig's method of detecting carbamide is unsuitable, but Fosse's method (A., 1914, ii, 756) gives trustworthy results, is not affected by the presence of ammonium salts, and allows the isolation of carbamide by the action of alcoholic hydrogen chloride on the dioxanthylcarbamide.

Attempts have also been made to effect the oxidation of ammonium carbamate to carbamide by purely chemical means; hydrogen peroxide or calcium permanganate gives small but distinctly recognisable quantities of carbamide. Oxidation may also be effected by ozone, either by leading ozonised oxygen into ammonium carbamate solution or over powdered ammonium carbonate, or by mixing ozonised oxygen, ammonia, and carbon dioxide. The yield depends on the concentration of ammonia and the temperature. The chemical and electrochemical oxidations have the transformation of ammonia into ammonium nitrate as a common feature; also, the local increase in temperature caused by the reaction is sufficient to cause a purely thermal transformation of ammonium carbamate into carbamide.

The general explanation of the equilibrium between ammonium carbamate and carbamide is that the former passes into the latter by loss of a molecule of water. This, however, is opposed to the law of mass action; the change is more probably represented by the scheme:  $\text{NH}_4\cdot\text{CO}_2\text{NH}_4 + \text{H}_2\text{O} \rightleftharpoons (\text{NH}_4)_2\text{CO}_3 = \text{CO}(\text{NH}_2)_2 + 2\text{H}_2\text{O}$ . Direct experiment shows that the rate of formation of carbamide is increased by water in the early stages of the reaction, as is required by the above hypothesis. The authors are therefore led to the conclusion that normal ammonium carbonate is the

actual source of carbamide; since, however, the presence of water has an effect disadvantageous to the carbamide in the final equilibrium,  $(\text{NH}_4)_2\text{CO}_3 \rightleftharpoons \text{CO}(\text{NH}_2)_2 + 2\text{H}_2\text{O}$ , it is advisable to operate with substances containing the components of ammonium carbonate, but having less water, such as ammonium carbamate. At the temperature of the reaction, the small quantity of hygroscopic moisture is sufficient to start the conversion of the carbamate into carbonate, and as soon as the latter commences to be transformed into carbamide, water is liberated in amount sufficient to complete the hydration of the carbamate. In the anhydrous condition, ammonium carbamate is more stable than the carbonate; in the presence of water, however, it becomes unstable, and, above a certain temperature, is incapable of existence. In the region above  $135^\circ$ , there is only the equilibrium between ammonium carbonate and carbamide, in which the latter is favoured by further rise of temperature; below  $135^\circ$ , on the other hand, the complex equilibrium of the first scheme exists. The maximum yield obtained at  $135^\circ$  thus finds a simple explanation. The equilibrium,  $(\text{NH}_4)_2\text{CO}_3 \rightleftharpoons \text{CO}(\text{NH}_2)_2 + 2\text{H}_2\text{O}$ , has been investigated at  $125^\circ$ ,  $100^\circ$ ,  $78^\circ$ , and  $37\text{--}38^\circ$ , and the combined effects of temperature and dilution are explicable from the point of view of the complex equilibrium scheme. Lowering of temperature renders the carbamate and the carbamide more stable; increase in the quantity of water acts in the opposite direction in each case. According to the preponderance of one or the other factors, the following effects may be observed at temperatures below  $135^\circ$  with a constant molecular ratio of carbamate to water: (1) the second portion of the scheme may be so far favoured that the yield of carbamide is increased, since the amount of water suffices to convert a larger proportion of carbamate into carbonate in spite of the actual increased stability of the former; (2) the yield may remain constant, since the increase in stability of the carbamate balances the increased tendency to formation of carbamide; (3) the increased stability of the carbamate is not counterbalanced by the amount of water, and the yield of carbamide sinks. All three possibilities have been experimentally realised. Free ammonia favours the carbamide in the equilibrium,  $(\text{NH}_4)_2\text{CO}_3 \rightleftharpoons \text{CO}(\text{NH}_2)_2 + 2\text{H}_2\text{O}$ , in the absence of water, but is without influence in presence of the latter.

H. W.

**Acetylmethylcarbamide.** ROBERT BEHREND and HANS ODENWALD (*Annalen*, 1918, **416**, 228—229).—Fifty-nine grams of acetamide (1 mol.) are dissolved in 88 grams of bromine (0.55 mol.), a 20% solution of potassium hydroxide (56 grams; 1 mol.) is added, the solution is heated on the water-bath until it becomes yellow and is no longer alkaline, and is then cooled, when acetylmethylcarbamide crystallises. Further quantities can be obtained from the mother liquor, the total yield being 75% of the theoretical. With even a slight excess of alkali, the yield falls to zero. C. S.

**Substitution in Aromatic Compounds.** H. J. PRINS (*Chem. Weekblad*, 1918, 15, 571—580).—It has been shown in an earlier paper (*ibid.*, 98) that substitution in aromatic compounds begins by addition to a carbon atom of the ring, followed by reaction with the hydrogen atom attached to that carbon atom; the reactivity of the hydrogen atom depends, therefore, in the first place, on the degree of unsaturation of the atom to which it is attached, as is true also in the case of alcohols and amines. Since unsaturation is distributed over the whole nucleus, addition can obviously occur at more than one carbon atom. The analogy with alcohols and amines is shown, not only in the carbon atoms of the nucleus, but in oxygen or nitrogen atoms in side-chains attached to the nucleus, and substitution can be brought about in all these cases by the same catalysts.

Substitution may be not only direct, but indirect also, as in the case of chloroacetanilide; the reaction here is unimolecular, and may be ascribed to a disturbance of the equilibrium between the energy of the atoms (atom-energy) and the energy of combination between the atoms (link-energy). Substitution occurs, then, in the first place at the least saturated carbon atom, but this may not yield the most stable system, and the substituting group may finally take up a different position.

The entry of any substituent X into the benzene ring must cause a change in the relation between atom-energy and link-energy, both in the substituent and in the nucleus. Two cases may arise. In the first, in which the link-energy between X and C<sub>1</sub>, the carbon atom to which X becomes attached, is greater than that between C<sub>1</sub> and the hydrogen atom displaced; the atom-energy of C<sub>1</sub> is therefore reduced, and to restore this as far as possible, the link-energy between C<sub>1</sub> and its neighbours, C<sub>2</sub> and C<sub>6</sub>, is reduced, with the consequence that the link-energy between C<sub>2</sub> and C<sub>4</sub> and between C<sub>3</sub> and C<sub>5</sub> is increased (C<sub>4</sub> and C<sub>5</sub> being the neighbours of C<sub>2</sub> and C<sub>3</sub> remote from C<sub>1</sub>), and that between C<sub>4</sub> and C<sub>6</sub> and C<sub>5</sub> and C<sub>6</sub> is diminished; C<sub>6</sub>, therefore, by the diminution of its link-energy, receives an increase of atom-energy, and is therefore rendered more reactive. The effect of introducing X, therefore, is to make the para-carbon atom more reactive. In the second case, in which the link-energy between C<sub>1</sub> and the substituent is less than between C<sub>1</sub> and hydrogen, the redistribution of energy causes an increase in the atom energy of C<sub>4</sub> and C<sub>5</sub>, that is, of the carbon atoms in the meta-position.

The fact that a substituent which directs a second substituting group to the meta-position also causes a reduction in the velocity of substitution is taken to indicate that the atom-energy of the atoms of the substituted nucleus is less than that of the atoms of the unsubstituted benzene ring itself, and hence it follows that the introduction into the ring of a group which directs to the meta-position causes the transformation of atom-energy into link-energy throughout the ring as a whole.

It is shown that substitution in the benzene ring cannot be explained by the assumption of a conjugated system, as attempted by Böseken (A., 1912, i, 430) and by Holleman (*Chem. Weekblad*, 1913, 10, 615, 618), without postulating many other conditions.

S. I. L.

**Pyrogenic Acetylene Condensations.** V. RICHARD MEYER and WILHELM MEYER (*Ber.*, 1918, 51, 1571—1587. Compare A., 1917, i, 313).—In addition to the substances previously identified in the product of the pyrogenic condensation of acetylene, *o*-xylene (identified as *o*-phthalic acid) and indene have been detected and the presence of mesitylene and  $\psi$ -cumene confirmed. Durene and isodurene could not be detected. The methylthiophen obtained by the condensation of acetylene, methane, and hydrogen sulphide (*loc. cit.*) is proved to be  $\alpha$ -thiotolene, and thionaphthen has been found in the product of the condensation of acetylene and hydrogen sulphide. A complete list is given of all the products obtained by pyrogenic acetylene condensations.

Hydrindene brominated in the cold in the presence of a little iodine yields 4:5:6:7-tetrabromohydrindene,  $C_6Br_4 \begin{smallmatrix} <CH_2> \\ <CH_2> \end{smallmatrix} CH_2$ , needles, m. p. 200° (which is converted into tetrabromophthalic acid by oxidation), but, brominated in boiling chloroform, yields 1:2:3-tribromohydrindene, feathery crystals, m. p. 134°, which yields phthalic acid by oxidation, and is also obtained by the further bromination of indene dibromide.

About 0.5 c.c. of aniline was obtained when the vapour of 3 litres of benzene mixed with ammonia was passed during twenty-four hours through a tube heated at 550° initially and at 700° finally; aniline could not be detected if the temperature was maintained at 550° throughout. [See also *J. Soc. Chem. Ind.*, 1919, 35A.]

C. S.

**The Optically Active neoMethylhydrindamines.** JOSEPH WALTER HARRIS (*T.*, 1919, 115, 61—67).

**The Fusion of Sodium Hydroxide with Several Phenols and Sulphonic Acids.** MAITLAND C. BOSWELL and J. V. DICKSON (*J. Amer. Chem. Soc.*, 1918, 40, 1786—1793).—A number of experiments were carried out in which sodium benzene sulphonate was fused with sodium hydroxide at temperatures of 300—350° in a closed vessel in presence or absence of air, the gaseous contents of the tube being analysed before and after the experiments. It was found that when the fusion was carried out in presence of air, a considerable quantity of hydrogen was formed and a much smaller quantity of methane or other gaseous hydrocarbon. At the same time, some of the oxygen originally present disappeared, the volume ratio of hydrogen formed to oxygen used up being approximately 1:2. When air is excluded from the fusion, however, no hydrogen or methane appears. It was found working on comparatively large quantities of material, that b

carrying out the fusion in an atmosphere of nitrogen instead of air, the yield of phenol could be increased from 90% to 98% of the theoretical.

In the presence of free oxygen, secondary reactions evidently occur involving the absorption of oxygen, followed by an oxidation involving the elements of water. To determine whether any of the dihydroxy- or trihydroxy-benzenes are formed as secondary products, the fusion of all six of these with sodium hydroxide in presence or absence of air was studied. In the case of five of them, hydrogen was formed in presence, not in absence of air. In the case of hydroxyquinol, much hydrogen is evolved even in absence of air, and also considerable quantities of methane. It is not considered that any of these can be the direct cause of hydrogen formation in the benzenesulphonate fusion.

Sodium hydroxide does not bring about catalytic oxidation of the dihydroxybenzenes, of pyrogallol, of  $\beta$ -naphthalenesulphonic acid, or phenylglycine- $\alpha$ -carboxylic acid. With sodium anthraquinone- $\beta$ -sulphonate, however, oxidation occurs in absence of oxygen, with formation of free hydrogen. E. H. R.

**The Miscibility of Phenol and Alkaline Solutions.** RENÉ DUBRISAY, TRIPIER, and TOQUET (*Compt. rend.*, 1918, 167, 1036—1038).—The coefficient of reciprocal miscibility of phenol and water steadily increases with the addition of alkali hydroxides to the water. Curves are given for sodium hydroxide at concentrations varying from  $N/20$  to  $N/3$ . The action of the alkaline earth hydroxides is similar, but less marked. On the other hand, acids and salts of the strong acids cause a diminution in the coefficient, and the same holds good for the alkali carbonates.

W. G.

**Aromatic Derivatives of Orthosulphurous Acid.** M. M. RICHTER (*Annalen*, 1918, 416, 291—304. Compare A., 1917, 24).—The attempt to prepare aryl sulphates in the same way as aryl sulphites (*loc. cit.*) by means of sulphuryl chloride and uridine failed, chlorinated liquid products being obtained. Phenyl sulphate is obtained indirectly by dissolving phenyl sulphite in concentrated sulphuric acid with cooling and pouring the solution into water. The amorphous precipitate obtained separates from formic acid solution in plates with blunted angles, m. p.  $83^\circ$  (decomp.; rapidly heated) or  $280$ — $282^\circ$  (decomp.; slowly heated). The substance is regarded as a double salt of diphenyl sulphate (1 mol.) and diphenyl sulphite (2 mols.) having the formula  $\text{SO}_2\text{O}:\text{S}(\text{OPh})_3$ , that is, it is a sulphate of triphenyl-orthosulphurous acid. It is easily soluble in formic, sulphuric, and phosphoric acids, in methyl sulphate and in alkali hydroxides and carbonates, ammonia and alkali sulphides, dissolves slightly in warm methyl or ethyl alcohol and in boiling water, and is insoluble in all other common solvents. It is converted by alcoholic hydrochloric acid at  $70^\circ$  into the chloride of triphenyl-orthosulphurous acid,  $\text{S}(\text{OPh})_3\text{Cl}$ , long, prismatic needles, m. p.  $256^\circ$  (decomp.), and a dilute potassium hydroxide solution by a solution of pyridine



hydrochloride containing an excess of pyridine into *triphenylorthosulphurous acid*,  $\text{OH}\cdot\text{S}(\text{OPh})_3$ , an amorphous powder, m. p.  $233^\circ$ . The last substance is amphoteric. Its acidic character is weaker than that of carbonic acid, whilst its basic properties are such that a hot 50% alcoholic solution has an alkaline reaction towards litmus. The three phenyl groups are not eliminated by hydrolysing agents. By treating an alcoholic suspension of the acid with the requisite acid, the *bromide*,  $\text{S}(\text{OPh})_3\text{Br}$ , needles, m. p.  $241\text{--}242^\circ$  (decomp.), *iodide*, short needles, m. p.  $194\text{--}195^\circ$  (reddening), *nitrate*, hair-like needles, m. p.  $160\text{--}161^\circ$  (decomp.), *acetate*, waxy mass, and *picrate*, yellow mass, are obtained. *Ethyl triphenylorthosulphite*,  $\text{OEt}\cdot\text{S}(\text{OPh})_3$ , amorphous powder, m. p.  $244^\circ$  (decomp.), is obtained from the chloride and alcoholic sodium ethoxide.

The *sulphate*,  $\text{SO}_2[\text{O}\cdot\text{S}(\text{O}\cdot\text{C}_6\text{H}_4\text{Me})_3]_2$ , crystals, m. p.  $296^\circ$  (decomp.), prepared from di-*o*-tolyl sulphite, and the corresponding *sulphate*, m. p.  $315^\circ$  (decomp.), prepared from di-*m*-tolyl sulphite, are obtained in the same way as the phenyl analogue; the latter yields *tri-m-tolylorthosulphurous acid*, amorphous powder, m. p.  $267^\circ$  (decomp.), by treatment with pyridine hydrochloride as above.

The colourless, amorphous *sulphate*, m. p.  $232^\circ$  (decomp.), obtained by pouring a solution of dithymyl sulphite in concentrated sulphuric acid into water, is regarded as a mixed anhydride of sulphuric, dithymylorthosulphurous, and trithymylorthosulphurous acids,  $(\text{C}_{10}\text{H}_{13}\text{O})_3\text{S}\cdot\text{O}\cdot\text{SO}_2\cdot\text{O}\cdot\text{S}(\text{O}\cdot\text{C}_{10}\text{H}_{13})_2\cdot\text{OH}$ . It is soluble in alcohol, but by treating its solution in aqueous-alcoholic potassium hydroxide with alcoholic sulphuric acid, a *sulphate*,  $\text{SO}_2[\text{O}\cdot\text{S}(\text{O}\cdot\text{C}_{10}\text{H}_{13})_3]_2$ , amorphous powder, m. p.  $280\text{--}281^\circ$  (decomp.), is precipitated, which is insoluble in alcohol. The insoluble sulphate yields *trithymylorthosulphurous acid*, amorphous powder, m. p.  $274\text{--}275^\circ$  (decomp.), by the pyridine hydrochloride method, whilst the soluble sulphate, by treatment with alcohol and the requisite acid, yields the *chloride*,  $\text{SCl}(\text{O}\cdot\text{C}_{10}\text{H}_{13})_3$ , amorphous powder darkening at  $295\text{--}300^\circ$  without melting, *bromide*, small crystals, decomp.  $330\text{--}340^\circ$ , *iodide*, crystals, and *nitrate*, small rectangular plates blackening at  $285\text{--}290^\circ$  without melting.

C. S.

**Thiophenol in Synthetic Phenol.** G. CAPPELLI (*Gazzetta*, 1918, **48**, ii, 107—113).—The repulsive odour exhibited by some samples of synthetic *p*-enol is sometimes attributed to the presence of thiophen in the benzene used in the manufacture. The author shows that such odour is due to a small proportion of thiophenol formed from particles of sodium benzenesulphonate which, during the fusion with alkali, escape contact with the latter and undergo deoxidation at the surface of the iron in the manner observed by Stenhouse (*Annalen*, 1866, **140**, 284; 1869, **149**, 42). The phenol may be freed from this impurity by fusing it, adding a little alcohol to keep it liquid, and then adding, per kilo. of phenol, about 50 c.c. (more, if continued formation of precipitate shows it to be neces-

sary) of 10% alcoholic mercuric chloride solution. The excess of mercuric chloride is eliminated by leaving the clear liquid for a couple of days in contact with copper turnings or foil; the mercury deposited on the latter may be recovered by distillation. Fractional distillation of the decanted solution gives: (1) below 179°, water and alcohol, and (2) at 179–183°, pure phenol with its characteristic odour.

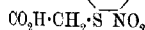
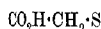
T. H. P.

**Organic Salts of Bivalent Chromium.** G. SCAGLIARINI (*Atti R. Accad. Lincei*, 1918, [v], 27, ii, 87–89; *Gazzetta*, 1918, 48, ii, 148–150).—The greyish-green salt obtained by Calcagni (*A.*, 1913, i, 1154) either from chrome alum and sodium salicylate or from chromic hydroxide and salicylic acid, and regarded by him as a chromous compound, is probably a salt of trivalent chromium in which also the phenolic hydroxyl groups take part in the salt-formation. All other chromous salts of organic acids, including those now described by the author, are red.

*Chromous salicylate*,  $C_6H_4 \begin{smallmatrix} \diagup CO \cdot O \\ \diagdown O \end{smallmatrix} Cr_3H_3O$ , prepared by reducing chrome alum solution with zinc and hydrochloric acid and adding sodium salicylate solution free from air, forms small, red crystals, but rapidly oxidises and becomes greenish-grey in the air.

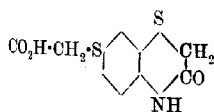
*Chromous propionate*,  $2(C_2H_5O_2)_2Cr.H_2O$ , was also prepared and analysed, and the butyrate and valerate prepared. T. H. P.

**Nitro-2:4-phenylenedithioglycollic Acid and Some of its Colouring Derivatives.** C. FINZI and N. BOTTIGLIERI (*Gazzetta*, 1918, 48, ii, 113–122).—The authors have prepared the nitro-derivative of *m*-phenylenedithioglycollic [*m*-phenylenedithiolacetic] acid, and as this yields on reduction, not an amino-acid, but a ketothiazine derivative, the conclusion is drawn that the nitro-group enters the benzene nucleus in the ortho-position to one of the substituents. The sulphone corresponding with the nitro-compound undergoes ring-closure on reduction still more easily, the resultant compound being quite analogous to Clausz's sulphazone (*A.*, 1912, i, 389), and being hence termed sulphazon-sulphonacetic acid. This acid has been coupled with various diazo-compounds, the derivatives thus obtained being of different colours and serving as substantive dyestuffs for silk.



4-Nitro-*m*-phenylenedithiolacetic acid (annexed formula), obtained from *m*-phenylenedithiolacetic acid and nitric acid, forms slender, yellow needles, m. p. 174°.

2-Keto-2:3-dihydrothiazine-6-thiolacetic acid (annexed formula),

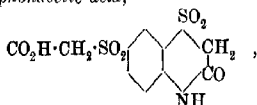


obtained by reducing the previous compound, forms tufts of silky, white needles, m. p. 210°; its sodium salt (+ 3H<sub>2</sub>O) was prepared and analysed.

4-Nitro-*m*-phenylenedisulphonacetic acid,  $NO_2 \cdot C_6H_3(SO_2 \cdot CH_2 \cdot CO_2H)_2$ , prepared by the action of hydrogen per-

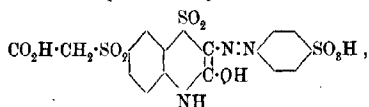
oxide on the nitro-acid, forms long, white needles, m. p. 199° (decomp.). On reduction with tin and hydrochloric acid, it yields

*Sulphazon-6-sulphonacetic acid*,

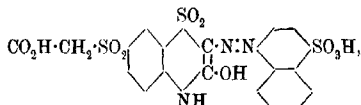


which forms white, mammillary masses of slender needles, m. p. 219° (decomp.).

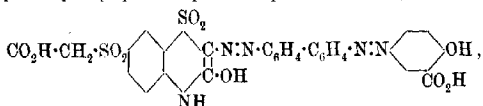
*p-Sulphobenzeneazosulphazon-6-sulphonacetic acid*,



obtained by condensing the preceding acid with diazobenzene-sulphonic acid, forms small needles of the colour of chromic anhydride. At 40–50° in aqueous solution, it is fixed directly on silk, giving a brilliant orange-yellow colour stable against soap and light; wool fixes it with more difficulty, but assumes a stable, yellow coloration. *4-Sulphonaphthaleneazosulphazonacetic acid*,



dyes silk an old-gold yellow stable against soap and light. *Salicylic-acid-p-azodiphenyl-p'-azosulphazonsulphonacetic acid*,

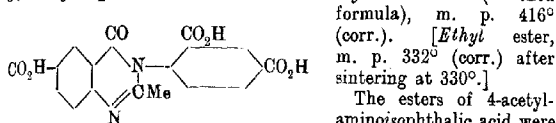


forms a brownish-black colouring matter almost insoluble in water, and directly colours silk yellow with an olive-green tinge.

T. H. P.

**4-Aminoisophthalic Acid and its Derivatives.** RUDOLF WEGSCHEIDER, HANS MALLE, ALFRED EHRLICH, and ROBERT SKUTEZKY (*Monatsh.*, 1918, **39**, 375–417).—4-Acetylaminoisophthalic acid is conveniently prepared by oxidising 4-acetoxylidide with a boiling aqueous solution of calcium permanganate; when rapidly heated, it becomes yellow at about 270°, melts at 295–296° (corr.; decomp.), immediately resolidifies, and then remains unchanged up to 350°; when slowly heated, decomposition frequently occurs without visible liquefaction. (The calcium salt

[+3H<sub>2</sub>O] is described.) During the heating, one molecule of acid loses its acetyl group, and the residue reacts as an amine with a second molecule of acid, yielding thereby 4-*keto*-3-*phenyl*-2-*methyl*-3:4-*dihydroquinazoline*-6 : 2' : 4'-*tricarboxylic acid* (annexed



The esters of 4-acetyl-aminoisophthalic acid were prepared by acetylation of the corresponding esters of the amino-acid: *methyl 4-acetyl-aminoisophthalate* has m. p. 125—126°; *1-methyl 3-hydrogen 4-acetylaminoisophthalate* melts at 218—219°; the corresponding normal and acid ethyl esters have m. p.'s 109—110° and 193.5—194.5° respectively. Attempts to esterify the acetylaminophtalic acid by methyl alcohol and mineral acids led, as in the case of acetylaminoterephthalic acid (Wegscheider and Faltis, A., 1912, i, 463) to the deacetylation of the acid.

4-Aminoisophthalic acid is most conveniently prepared from its acetyl derivative by esterifying the latter with methyl alcohol and mineral acid, and subsequent hydrolysis of the purified amino-ester so formed; it has m. p. 336—337° (corr.; decomp.). The *dimethyl* and *diethyl* esters have m. p.'s 131.5° and 79—80° respectively, whilst *1-methyl 3-hydrogen 4-aminoisophthalate* and the corresponding *ethyl* ester melt at 224—225° (decomp.) and 216.5—218°. The acid behaves contrary to the usual rule, since it yields the same ester by treatment with mineral acid and methyl alcohol and by half-hydrolysis of the normal ester.

The methylation of the amino- and acetyl-amino-acids and their esters has been studied under varying conditions. 4-*Dimethyl-aminoisophthalic acid* is most conveniently prepared by treatment of the corresponding dimethyl ester with methyl sulphate at 100° and hydrolysis of the ester (m. p. 70°) with alcoholic potassium hydroxide; its m. p. depends greatly on the mode of heating. The silver salt is described. Methylation of the free acid is very incomplete either by the action of methyl sulphate on the dry potassium salt in the presence of potassium hydroxide solution or in the presence of water and barium carbonate. The use of methyl iodide and potassium hydroxide does not lead to better results. 4-Acetylaminoisophthalic acid is methylated with still greater difficulty, yielding small amounts of dimethylaminoisophthalic acid. Methyl sulphate does not act on dimethyl 4-acetylaminoisophthalate below 115°; at 120—124°, however, *trimethyl 4-keto-3-phenyl-2-methyl-3 : 4-dihydroquinazoline*-6 : 2' : 4'-*tricarboxylate*, m. p. 205.5°, is produced.

4-Acetyl*methylaminoisophthalic acid* is prepared by the action of methyl iodide on the sodium or, preferably, the potassium salt of dimethyl 4-acetylaminoisophthalate and subsequent hydrolysis with alcoholic potassium hydroxide solution; it forms colourless

needles, the m. p. of which depends on the mode of heating. 4-Methylaminoisophthalic acid has m. p. 297·5—298·5° (corr.) after decomposition at 296° when placed in a bath preheated to 293°; the corresponding dimethyl ester melts at 115°. 1-Methyl-3-hydrogen 4-methylaminoisophthalate, m. p. 238—239° (decomp.), is obtained by the partial esterification of 4-methylaminoisophthalic acid with methyl alcohol and hydrogen chloride. H. W.

**Colour and Chemical Constitution. III. Derivatives of the Unknown *op*-Phenolphthalein.** JAMES MOIR (*Trans. Roy. Soc. S. Africa*, 1918, 7, 123—127. Compare A., 1917, ii, 349, 557).

—The preparation and absorption spectra of a number of phthalein derivatives containing one hydroxyl group in the *ortho*- and a second in the *para*-position to the central carbon atom are described. Thus *phenol-p-cresolphthalein* is obtained by heating a mixture of *p*-cresol and *p*-hydroxybenzoylbenzoic acid in the presence of zinc chloride. The following substances are prepared in a similar manner: *op-phenolphthalein-m-carboxylic acid* and its methyl ether, *hydroxydiphenylphthalidecarboxylic acid*, *m-amino-op-phenolphthalein*, the corresponding *m-methylamino-derivatives* and its *ω-carboxylic acid*, *m-phenyl-op-phenolphthalein*, and *m-nitro-op-phenolphthalein*. Attempts to prepare *op-phenolphthalein* by reduction of *m-ido-op-phenolphthalein* did not yield the desired result, and further work in this direction was abandoned, since it was discovered that *p*-hydroxybenzoylbenzoic acid yields a phthalein-like substance when heated at above 200°, or at a lower temperature in the presence of concentrated sulphuric acid; this substance, which resembles phenolphthalein very closely, can also be obtained by heating phenolphthaleinoxime with a small quantity of sulphuric acid at above 200°, and it therefore appears probable that the so-called oxime is in reality the *p*-hydroxyanilide of *p*-hydroxybenzoylbenzoic acid.

It is possible to find a particular strength of alkali in which any phthalein gives a colourless solution in the cold, but which becomes coloured on heating to near the boiling point, and again fades on cooling and keeping. For ordinary phenolphthalein, the concentration of alkali is slightly above normal; tetraiodophenolphthalein requires a much weaker alkali, whilst *α*-naphtholphthalein requires about 2*N*-alkali.

Phenolphthalein-*o*-carboxylic acid is coloured faintly pink by ammonia and deep violet-pink by alkali hydroxide; as an indicator, it resembles thymolphthalein, but has a more favourable colour. The corresponding dicarboxylic acid is useful in proving the presence of definite caustic alkalinity at about *N*/100.

H. W.

**Constitution of the Hydrazone of Benzaldehyde.** J. SUREDA BLANES (*Anal. Fis. Quim.*, 1918, 16, 707—718).—The author summarises the evidence for and against the cyclical formula of Curtius for the aliphatic diazo-compounds,  $RR\cdot C \begin{smallmatrix} \diagup N \\ \diagdown N \end{smallmatrix}$ , as com-

pared with the lineal formula,  $RR \cdot C:N:N$ , suggested by Angeli and later by Thiele.

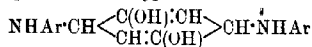
The easy oxidation of hydrazones to diazo-compounds suggests the investigation of the constitution of the former substances. The hydrazone chosen for preliminary examination is that of benzaldehyde, which on oxidation gives phenyldiazomethane. The alternative structures which may be assigned to benzaldehydehydrazone are:  $CHPh \begin{smallmatrix} NH \\ \diagdown \\ NH \end{smallmatrix}$  and  $CHPh:N \cdot NH_2$ .

The following reactions establish the latter formula:

- (1) Benzaldehydehydrazone and phenylcarbimide,  
 $CHPh:N \cdot NH_2 + CONPh = NHPh \cdot CO \cdot NH:N \cdot CHPh$ .
- (2) Benzaldehydehydrazone and phenylthiocarbimide,  
 $CHPh:N \cdot NH_2 + SCNPh = NHPh \cdot CS \cdot NH:N \cdot CHPh$ .
- (3) Benzaldehydehydrazone and diphenylketen,  
 $CHPh:N \cdot NH_2 + CPh_2 \cdot CO = CHPh_2 \cdot CO \cdot NH:N \cdot CHPh$ .

The product of the last reaction forms white crystals insoluble in alcohol, ether, or benzene, slightly soluble in light petroleum and glacial acetic acid, m. p. 196°. These reactions are incompatible with the cyclical formula for benzaldehydehydrazone, and therefore the lineal formula must be assumed. W. S. M.

**Anilinoquinones.** HERMANN SUIDA and WILHELM SUIDA (*Annalen*, 1918, **416**, 113—163).—The generally accepted view that anilinoquinones are always formed by the transformation of an additive compound of the type



into  $NHAr \cdot C \begin{smallmatrix} < CO \cdot CH \\ > CH \cdot CO \end{smallmatrix} > C \cdot NHAr$ , with the removal of four atoms of hydrogen, which reduce two further molecules of the quinone, is found not to hold. In some cases, the reaction recognisably passes through the monoanilide. In the case of the simplest and most reactive components, monoanilides are smoothly formed in accordance with the equation  $2C_6H_4O_2 + NH_2Ar = C_6H_3O_2 \cdot NHAr + C_6H_4(OH)_2$ . The capacity of the group  $\cdot CO \cdot CH \cdot CH \cdot CO \cdot$  to form anilino-compounds must be connected in some way with the structure of the benzene nucleus, because maleic and fumaric esters and the *cis*- and *trans*-modifications of dibenzoylethylene, in which this group occurs, do not react in this way with aromatic amines.

Under the conditions of the authors' experiments, the following generalisations have been made. *p*-Benzoquinone in aqueous, faintly acetic acid solution yields with all pronouncedly basic primary and secondary aromatic amines anilinoquinones, predominantly and even sometimes exclusively monoanilinoquinones. The intensity of the reaction diminishes as the basic character of the amine is weakened by the entrance of acidic substituents. Thus the strongest bases (aniline and its homologues, diamines, etc.) yield mono- and di-anilides simultaneously, the weaker bases (secondary amines, nitroanilines, etc.) yield only monoanilides,

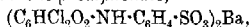
whilst the weakest bases do not react in aqueous solution. Tolu-quinone yields only monoanilides, and *s*-xyloquinone does not react.

In alcoholic solution, *p*-benzoquinone forms only dianilides; monoanilides are present in the mother liquor only when the basic component contains acidic substituents. Tolu- and naphth-quinones yield only monoanilides, and *s*-xyloquinone none.

The reactions also proceed in glacial acetic acid solution. Therefore by a suitable selection of the solvent and of the temperature it is possible to make a quinone react once or twice with an amine, or a monoanilinoquinone to react with a different base, producing a mixed dianilinoquinone.

The following new derivatives of *p*-benzoquinone have been prepared: 5-*anilino*-2-*a-naphthylamino*-,  $C_{22}H_{16}O_2N_2$ , yellowish-brown powder, m. p. 278–280°; 2-*p-chloroanilino*-, sepia crystals, decomp. about 115°; 2:5-*di-p-chloroanilino*-, pale brown crystals; 2-*o-toluidino*-, dark violet-brown crystals, m. p. 100–104°; 2:5-*di-o-toluidino*-, rust-red needles, m. p. 250–252°; 2-*m-toluidino*-, dark violet-brown crystals, m. p. 90–100° (decomp.); 2:5-*di-m-toluidino*-, crimson-red needles, m. p. 256–257°; 2-*p-toluidino*-, aggregates of violet-black needles, m. p. 134–137° (bath at 134°); 2:5-*di-p-toluidino*-, crystals, m. p. 318°; 2-*acetylaminooanilino*-, dark crystals; 2-*as-m-xylidino*-, reddish-brown crystals, m. p. 102°; 2:5-*di-as-m-xylidino*-, pale brown crystals, m. p. 297–300°; 2-*ψ-cumidino*-, brick-red crystals, m. p. 90–106°; 2:5-*di-ψ-cumidino*-, pale red crystals, m. p. 301–303°; 2-*o-anisidino*-, brownish-violet leaflets with metallic lustre, m. p. 114° (not sharp).

With the object of preparing monoanilides soluble in water, the aminobenzenesulphonic acids have been utilised. These do not react satisfactorily with *p*-benzoquinone, but give good results with the less reactive 2:6-dichloro-*p*-benzoquinone. By adding to a hot alcoholic solution of this a hot aqueous solution of sulphanilic acid (1 mol.), and subsequently an aqueous solution of sodium acetate (1 mol.), and then barium chloride, *barium* 2:6-dichloro-5-*anilino-p-benzoquinone-p'-sulphonate*,



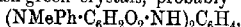
copper-red leaflets, is obtained, the mother liquor containing 2:6-dichloroquinol. If the temperature is about 60° at the beginning and about 30° at the end of the experiment, the product is mainly the *barium hydrogen* salt. An aqueous solution of the barium salt at 100° rapidly acquires chlorine ions and deposits a blackish-brown powder, which appears to be the *barium* salt of 2-chloro-5-*p-sulphoanilino*-6-hydroxy-*p-benzoquinone*. By adding sulphanilic acid to a hot aqueous solution of the first-mentioned barium salt, the *barium hydrogen* salt of 6-chloro-2:5-*dianilino-p-benzoquinone-p''-disulphonic acid* is obtained as a brownish-black powder.

2-Methyl-*anilino-p-benzoquinone*,  $C_9H_8O_2 \cdot NMePh$ , prepared by adding a cold 50% acetic acid solution of methylaniline (1 mol.) to an aqueous solution of *p*-benzoquinone (3 mols.), forms dark red

needles, m. p. 125—130°. 2:5-Dimethylanilino-*p*-benzoquinone, leaflets, m. p. 205°, is obtained from its components in alcoholic solution.

2-Methylanilino-*p*-benzoquinone, like all other monoanilinoquinones of the same type, yields mixed dianilinoquinones by trituration with an aromatic base or by warming with it in alcoholic solution. The following 2-methylanilino-*p*-benzoquinones of this kind have been prepared: 5-anilino-,  $\text{NMePh} \cdot \text{C}_6\text{H}_3\text{O}_2 \cdot \text{NHPh}$ , orange-red crystals; 5-*p*-carboxyanilino-, dark red leaflets; 5-*m*-carboxyanilino-, brownish-red crystals; 5-*m*-chloroanilino-, garnet-red needles; 5-*o*-hydroxyanilino-, brown leaflets; 5-*m*-hydroxyanilino-, brownish-yellow, metallic crystals; 5-*p*-bromoanilino-, red crystals; 5-*p*-sulphoanilino-, prepared in the presence of sodium carbonate and 3% hydrogen peroxide, and isolated as the sodium salt; 5- $\alpha$ -naphthylamino-, dark brown crystals; 5- $\beta$ -naphthylamino-, dark violet-brown crystals; 5-*p*-benzeneazoanilino-, violet-brown crystals.

2-Methylanilino-*p*-benzoquinone (2 mols.) and *p*-phenylenediamine (1 mol.) react in boiling alcohol to form a substance,  $\text{C}_{22}\text{H}_{20}\text{O}_4\text{N}_4$ , brownish-green crystals, probably

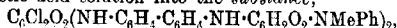


whilst in the ratio of 4:1, in alcohol, glacial acetic acid or nitrobenzene, or by moistening the mixture of the two components with a little solvent and warming on the water-bath, a dark green, crystalline substance,  $[(\text{NMePh} \cdot \text{C}_6\text{H}_3\text{O}_2)_2\text{N}]_2\text{C}_6\text{H}_4$ , is obtained, m. p. 250—260°.

2-Methylanilino-*p*-benzoquinone and benzidine react in warm alcohol to form the compound,

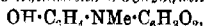


brown needles, m. p. 215—218°, which is converted by chloranil in glacial acetic acid solution into the substance,



crystals. 2-Methyl-*p*-toluidino-*p*-benzoquinone and *p*-phenylenediamine in hot alcoholic solution yield a dark green substance, probably  $(\text{C}_7\text{H}_7 \cdot \text{NMe} \cdot \text{C}_6\text{H}_3\text{O}_2 \cdot \text{NH})_2\text{C}_6\text{H}_4$ .

2-Ethylanilino-*p*-benzoquinone forms dark needles, m. p. 85° with previous sintering. 2-Benzylanilino-*p*-benzoquinone forms almost black needles, m. p. 60—70°, whilst 2:5-dibenzylanilino-*p*-benzoquinone,  $\text{C}_{24}\text{H}_{20}\text{O}_4(\text{NPh} \cdot \text{CH} \cdot \text{Ph})_2$ , crystallises in blood-red needles, m. p. 155—156°. 2-Methyl-*p*-toluidino-*p*-benzoquinone forms reddish-yellow needles, m. p. 127°, and 2:5-dimethyl-*p*-toluidino-*p*-benzoquinone, yellowish-brown, rhombic plates, m. p. 206°. 2-*o*-Hydroxymethylanilino-*p*-benzoquinone,



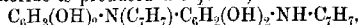
and 2:5-di-*o*-hydroxymethylanilino-*p*-benzoquinone are described.

A table is given of the colorations of the anilinoquinones in concentrated sulphuric acid. C. S.

**Polymerisation Phenomena in the Simple Monoanilino-benzoquinones.** HERMANN SUIDA (*Annalen*, 1918, 416, 164—181. Compare preceding abstract).—The monoanilinoquin-



ones derived from primary bases are only stable in the pure dry state; they polymerise in solution. Dianilinoquinones, and also monoanilinoquinones derived from secondary bases, show no tendency to polymerise. The polymerisation is probably represented thus:  $2C_6H_3O_2 \cdot NHAr \rightarrow C_6H_3O_2 \cdot NAr \cdot C_6H_3(OH)_2 \cdot NHAr$ ; the dimeric merquinonoid form produced can undergo further polymerisation. The polymerisation is brought about by heating the monoanilinoquinone at its m. p., by heating with water or dilute acetic acid, by prolonged boiling with alcohol, or by exposing its cold alcoholic solution to intense light. Thus 2-*p*-toluidino-*p*-benzoquinone yields the *dimeride*,  $(C_{13}H_{11}O_2N)_2$ , m. p. 265–267° (in carbon dioxide), from which by reduction with alcoholic stannous chloride is produced the *quinol*,



pale yellow crystals, m. p. 236–237° (in carbon dioxide). Dimeric *p*-toluidino-*p*-benzoquinone,  $C_6H_3O_2 \cdot N(C_2H_5) \cdot C_6H_3O_2 \cdot NH \cdot C_2H_5$ , produced by auto-oxidation by boiling the dimeric merquinone in glacial acetic acid or nitrobenzene, forms violet-black crystals with green lustre, which remain unchanged at 400°; the oxidation is also effected by ferric chloride in dilute alcoholic solution.

C. S.

#### Anilinoquinones from Benzoquinone and the Nitroanilines.

GUIDO MEYER and HERMANN SUDA (*Annalen*, 1918, 416, 181–188).—The nitroanilines do not react as easily as aniline with benzoquinone. In cold aqueous solution, a reaction between the nitroanilines and *p*-benzoquinone is only observed when the nitroaniline is used in the form of its hydrochloride in the presence of an excess of hydrochloric acid; in all three cases, reddish-brown, crystalline additive compounds separate after some hours, but if kept in contact with the mother liquor for several weeks change into the mononitroanilino-*p*-benzoquinones. The latter are obtained immediately from the nitroanilines and *p*-benzoquinone in boiling aqueous solution. 2-*m*-Nitroanilino-*p*-benzoquinone and the *p*-nitro-compound are dark brown and do not crystallise well. The *o*-nitro-compound is less readily obtained. All three compounds have indefinite m. p.'s between 290° and 300°, and develop with sulphuric acid a reddish-violet coloration, which turns blue on warming.

In cold alcoholic solution, a reaction occurs only between *m*-nitroaniline and *p*-benzoquinone, whereby the additive compound is formed. In hot alcoholic or, better, hot glacial acetic acid solution, the 2-*o*-dinitroanilino-*p*-benzoquinones, decomp. 310–360°, are obtained.

The nitroanilino- and dinitroanilino-*p*-benzoquinones are not attacked by mild reducing agents. Tin and hydrochloric acid convert the latter into phenylenediamines and aminoanilinoquinols, which could not be isolated. *p*-Nitroanilinobenzoquinone was reduced by tin and hydrochloric acid to a base, which was isolated as the *sulphate*,  $C_6H_3(OH)_2 \cdot NH \cdot C_6H_4 \cdot NH_2 \cdot 2H_2SO_4$ , prismatic needles; the base itself could not be isolated.

C. S.

**Action of the Isomeric Chloromethylanilines on Benzo- and Tolu-quinones.** HEINRICH TEUTSCHER (*Annalen*, 1918, **416**, 189—202. Compare Suida and Suida, this vol., i, 79).—The chloromethylanilines in aqueous, faintly acetic acid solution yield exclusively monoanilinoquinones with *p*-benzo- and tolu-quinones; as usual, a second molecule of the quinone is reduced to the quinol. Additive products could not be isolated, although they are undoubtedly formed. In alcoholic solution, *p*-benzoquinone yields dianilinoquinones, whilst toluquinone yields only the monoanilinoquinone; here again evidence (colour change) has been obtained of the intermediate formation of additive compounds. Toluquinone, being a weaker oxidising agent than *p*-benzoquinone, reacts more slowly with the aromatic bases. Of these, *o*-chloromethylaniline reacts most slowly and the *p*-compound most rapidly.

2-*p*-Chloromethylanilino-*p*-benzoquinone,  $C_6H_3O_2 \cdot NMe \cdot C_6H_4Cl$ , is a dark red, crystalline powder, m. p.  $145^\circ$ , the *m*-chloro-compound a reddish-brown powder, m. p.  $127^\circ$ , sintering at  $120^\circ$ , and the *o*-chloro-compound crystallises in pale red needles, m. p.  $133^\circ$  (decomp.), sintering at  $60^\circ$ . 4-*p*-Chloromethylanilino-toluquinone forms a dark red, crystalline powder with metallic lustre, m. p.  $156^\circ$  (from aqueous solution), and dark red needles, m. p.  $184^\circ$  (decomp.) (from alcoholic solution), and the *o*-chloro-compound red leaflets with metallic lustre, m. p.  $146^\circ$  (decomp.).

2:5-Di-*p*-chloromethylanilino-*p*-benzoquinone forms deep bronze leaflets with metallic lustre, m. p.  $223^\circ$ , the *m*-chloro-compound, deep yellow leaflets, m. p.  $198^\circ$ , and the *o*-chloro-compound, reddish-bronze leaflets with metallic lustre, m. p.  $258^\circ$ .

2:5-Di-2':4'-dichloromethylanilino-*p*-benzoquinone, which requires the presence of hydrogen peroxide for its quick preparation, forms brick-red leaflets, m. p.  $240^\circ$ . C. S.

**Citronellol.** H. J. PRINS (*Chem. Weekblad*, 1918, **15**, 1378—1380).—Distillation of citronellol yields two fractions, one with b. p.  $217$ — $219^\circ$  and the other with b. p.  $219$ — $221^\circ$ . The liquids probably contain isomerides, but these cannot be separated by fractionation.

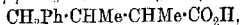
When free from geraniol and other substances, but containing these isomerides, citronellol of maximum purity should have  $D_{20}^{20}$  0.867—0.869, and its index of refraction should be  $n_D^{20}$  1.4586—1.4589. A. J. W.

**Constituents of Oil of Cassia. II.** FRANCIS D. DODGE (*J. Ind. Eng. Chem.*, 1918, **10**, 1005—1006. Compare A., 1916, i, 155).—Oil of cassia was found to contain cinnamaldehyde (75 to 90%), cinnamyl acetate, phenylpropyl acetate (?), *o*-methoxycinnamaldehyde, salicylaldehyde (0.1 to 0.2%), coumarin, benzoic acid, salicylic acid, an unidentified liquid acid, benzaldehyde, and *o*-methoxybenzaldehyde. [See, further, *J. Soc. Chem. Ind.*, 1919.] W. P. S.

### Constitution of Substances from Guaiacum Resin.

G. SCHROETER, L. LICHTENSTADT, and D. IRINEU (*Ber.*, 1918, 51, 1587—1613).—The milk test with extract of guaiacum resin is not entirely satisfactory, since it depends on the quality of the extract. Before examining the chemistry of the blue compound, it is necessary to determine the structure of the substance (or substances) in the resin which produces it.

The two substances of unknown constitution obtained by the dry distillation of guaiacum resin are guaiene and pyroguaiacin. The latter is known to be a hydroxymethoxy-derivative of the former (Herzig and Schiff, *A.*, 1897, i, 254; 1898, i, 327, 530). Guaiene is now proved to be 2:3-dimethylnaphthalene by synthesis. *β*-Phenylisopropyl bromide,  $\text{CH}_2\text{Ph}\cdot\text{CHMeBr}$ , b. p. 107°—109°/16 mm.,  $D^{16}_4$  1.2908, obtained from the alcohol and hydrobromic acid (saturated at 0°) at 100°, reacts with ethyl malonate and alcoholic sodium ethoxide on the water-bath to form *ethyl β-phenylisopropylmalonate*,  $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , b. p. 182°—183°/14 mm.,  $D^{16}_4$  1.0673. This is converted in the usual manner into *ethyl β-phenylisopropylmethylmalonate*, b. p. 188°/16 mm.,  $D^{16}_4$  1.0505, which yields the acid,  $\text{C}_{13}\text{H}_{16}\text{O}_4$ , colourless crystals, m. p. 158°—160° (decomp.), by hydrolysis. The acid, heated at 170°—190°, yields *γ-phenyl-αβ-dimethylbutyric acid*,



b. p. 179°—180.5°/13 mm., the acid chloride of which, b. p. 136°—143°/13 mm., is converted in light petroleum (b. p. 60°—70°) by aluminium chloride into 1-*keto*-2:3-dimethyl-1:2:3:4-tetrahydronaphthalene, b. p. 148°—150°/17 mm., m. p. -1°,  $D^{21}_4$  1.019. This is reduced by sodium and alcohol to 2:3-dimethyltetrahydronaphthol, m. p. 110°—114°, b. p. 148°—152°/18 mm., which loses water at above 200° and yields 2:3-dimethyl-Δ<sup>1</sup>-dihydronaphthalene, b. p. 120°—140°/16 mm., the dibromide of which is converted by boiling methyl-alcoholic potassium hydroxide into 2:3-dimethylnaphthalene, m. p. 104°—104.5° (picrate, m. p. 123°—124°), which is identical with guaiene.

Pyroguaiacin is converted by boiling alcoholic potassium hydroxide and methyl sulphate into *pyroguaiacin methyl ether*,  $\text{C}_{12}\text{H}_{10}(\text{OMe})_2$ , leaflets, m. p. 149°—150°, the oxidation of which by sodium dichromate and glacial acetic acid at 95°—115° yields *pyroguaiacinquinone methyl ether*,  $\text{C}_{14}\text{H}_{14}\text{O}_4$ , yellow needles, m. p. 241°—242°. For reasons given below, pyroguaiacin is almost certainly 6-hydroxy-7-methoxy-2:3-dimethylnaphthalene.

Guaiaretic acid, the extraction of which from guaiacum resin by ether is described in detail, has the formula  $\text{C}_{20}\text{H}_{24}\text{O}_4$  (Herzig and Schiff, *loc. cit.*, give  $\text{C}_{20}\text{H}_{24}\text{O}_4$ ), and is now found to be optically active,  $[\alpha]_D$  -94° in alcohol, and unsaturated. It is converted by methyl sulphate and hot aqueous-alcoholic potassium hydroxide into a *methyl ether*,  $\text{C}_{18}\text{H}_{18}(\text{OMe})_2$ , colourless needles, m. p. 94°—95°,  $[\alpha]_D$  -92° in alcohol, which is reduced by sodium and boiling alcohol or in solution in tetrahydronaphthalene at 180° by hydrogen and a nickel catalyst under a pressure of 40—50 kilog.

to *hydroguaiaretic acid methyl ether*,  $C_{15}H_{18}(OMe)_4$ ; in both cases a mixture of the *i*-acid, crystals, m. p. 100–101°, and the *l*-acid, flat prisms, m. p. 86–87°,  $[\alpha]_D - 27^\circ$  in alcohol, is obtained.

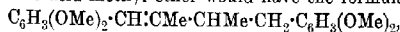
Herzig and Schiff's *norguaiaretic acid* (*loc. cit.*), obtained in poor yield from guaiaretic acid and boiling hydriodic acid, is obtained in much better yield from hydroguaiaretic acid methyl ether, and is reconverted into this by methylation; it is therefore *norhydroguaiaretic acid*.

*i*-Dibromohydroguaiaretic acid methyl ether,  $C_{15}H_{16}Br_2(OMe)_4$ , colourless needles, m. p. 130.5–131.5°, is obtained by the bromination of *i*-hydroguaiaretic acid methyl ether or guaiaretic acid methyl ether in glacial acetic acid, dehydroguaiaretic acid methyl ether (below) being also formed in the latter case. *l*-Dibromohydroguaiaretic acid methyl ether, colourless crystals, m. p. 121–122°,  $[\alpha]_D - 42^\circ$  in alcohol, is obtained by brominating *l*-hydroguaiaretic acid methyl ether.

*i*-Dinitrohydroguaiaretic acid methyl ether,  $C_{15}H_{16}(NO_2)_2(OMe)_4$ , yellow crystals, m. p. 150–151°, obtained by adding nitric acid, D 1.4, to *i*-hydroguaiaretic acid methyl ether or guaiaretic acid methyl ether in glacial acetic acid solution, is smoothly reduced in tetrahydronaphthalene solution by hydrogen and nickel to *i*-diaminohydroguaiaretic acid methyl ether, faintly violet needles, m. p. 124–125°; attempts to resolve this base by means of *d*-tartaric acid were unsuccessful. *l*-Dinitrohydroguaiaretic acid methyl ether, yellow crystals, m. p. 122–123°,  $[\alpha]_D - 49.5^\circ$  in glacial acetic acid, is obtained by the nitration of *l*-hydroguaiaretic acid methyl ether.

The reduction of *l*-guaiaretic acid and of its methyl ether yields a mixture of optically active and inactive hydro-derivatives, and therefore possibly racemisation has occurred. Since it is shown, however, that the hydro-derivatives racemise with great difficulty, an alternative explanation of the formation of the inactive modification is that a second carbon atom is rendered asymmetric by the reduction, the inactive hydro-derivative being internally compensated. In favour of the symmetric structure thus postulated is the formation of the probably symmetrically substituted dibromo- and dinitro-derivatives and the failure to resolve the diamino-derivative. Hydroguaiaretic acid methyl ether would therefore be *αβ*-diveratryl-*βγ*-dimethylbutane,

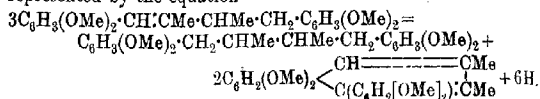
$C_6H_3(OMe)_2 \cdot CH_2 \cdot CHMe \cdot CHMe \cdot CH_2 \cdot C_6H_3(OMe)_2$ ,  
and guaiaretic acid methyl ether would have the formula



the positions of the two methyl groups being determined by the fact that guaiaretic acid can be converted through pyroguaiacin into guaiane (2:3-dimethylnaphthalene).

An extraordinary transformation of guaiaretic acid methyl ether is its *reduction* to hydroguaiaretic acid methyl ether by potassium permanganate in acetone-glacial acetic acid solution, veratric acid also being formed. The explanation is found in the action of Hübl's iodine solution on guaiaretic acid methyl ether (1 mol.),

whereby a mixture of *i*-hydroguaiaretic acid methyl ether and *dehydroguaiaretic acid methyl ether*,  $C_{22}H_{24}O_4$ , colourless crystals, m. p. 178.5—179°, optically inactive, is obtained in the proportion of 1:2 by the consumption of 1 mol. of iodine. This change is represented by the equation



It is probable, therefore, that in the preceding reaction with potassium permanganate, a portion of the guaiaretic acid methyl ether undergoes ring closure to a naphthalene derivative (which is then oxidised, yielding veratric acid and other products), the hydrogen produced reducing another portion to hydroguaiaretic acid methyl ether, which is stable towards permanganate.

By treatment with 2*N*-sodium hydroxide and methyl sulphate, guaiaconic acid yields a methyl ether, an amorphous, yellow powder, m. p. 94—102°, softening at 82°, which, unlike guaiaconic acid, does not develop a blue colour with lead peroxide. By oxidation with potassium permanganate in acetone-glacial acetic acid solution, the ether yields a comparatively large amount of veratric acid and other products, which were not identified.

Believing at first that guaiene was 1:2-dimethylnaphthalene, the authors synthesised this substance as follows. By treatment of their sodio-derivatives with methyl iodide in warm benzene, the  $\beta$ -phenylethylmalonic esters yield, respectively, *methyl  $\beta$ -phenylethylmethylmalonate*, b. p. 178—180°/18 mm., and the *ethyl ester*, b. p. 182—184°/12 mm., from which  $\beta$ -phenylethylmethylmalonic acid, colourless crystals, m. p. 150° (decomp.), is obtained. At 150—180°, the acid is converted into  $\gamma$ -phenyl- $\alpha$ -methylbutyric acid, b. p. 167°/11 mm., the acid chloride of which, b. p. 125°/12 mm., is converted in light petroleum solution by aluminium chloride into 1-*keto-2-methyl-1:2:3:4-tetrahydronaphthalene*, b. p. 127—131°/12 mm. This is converted by ethereal magnesium methyl iodide into 1-*hydroxy-1:2-dimethyl-1:2:3:4-tetrahydronaphthalene*, b. p. 135—140°/15 mm., m. p. 64—66°, which at 160—180° yields 1:2-dimethyl- $\Delta^1$ -dihydronaphthalene, b. p. 250—251°/atm. or 114—116°/15 mm.,  $D_{20}^{25} 0.9885$ ,  $n_D^{25} 1.5763$ . The *dibromide* of the latter, a pale yellow oil, is converted by boiling methyl-alcoholic potassium hydroxide into 2-methyl-1-methylene-3,4-dihydronaphthalene, b. p. 157°/15 mm., which yields 1:2-dimethylnaphthalene, b. p. 139—140°/15 mm. (*microt.*, orange-red crystals, m. p. 129.5—130.5°), by boiling with glacial acetic acid containing hydrogen chloride.

C. S.

**Classification of Organic Colouring Matters.** M. DOMINIKIEWICZ (*Chem. Zeit.*, 1918, **42**, 549—550, 562—564).—In the method of classification proposed, the substances are arranged under chief types depending on the constitution of the

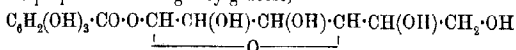
nucleus, these types being subdivided into classes. The types include the quinone type, the diphenylmethane type, the safranine type, the indigo type, etc. Sulphur derivatives and substances of unknown constitution form two separate classes. W. P. S.

#### Tannin and the Synthesis of Similar Substances. V.

EMIL FISCHER and MAX BERGMANN (*Ber.*, 1918, 51, 1760—1804. Compare A., 1912, i, 471, 887; 1913, i, 479; 1915, i, 437).—Previous attempts to prepare pentadigalloylglucose did not lead to the desired result, owing to the unfavourable properties of the methylcarbonato-compounds. Recently, however, it has been found possible to prepare the penta-acetyl derivatives of *m*- and *p*-digallic acids and the corresponding chlorides in the crystalline state (A., 1918, i, 172); from these, the penta-(penta-acetyldigalloyl)-glucoses have now been prepared, as well as the corresponding penta-(digalloyl)-glucoses. Penta-(*m*-digalloyl)- $\beta$ -glucose is shown to be remarkably similar to Chinese tannin, the only point of difference noted being in the specific rotation in aqueous solution. Since, however, the solutions are colloidal in character and their optical activity is greatly influenced by small factors, the authors do not consider the discrepancy is necessarily fundamental.

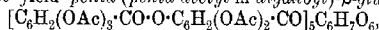
The chemistry of the pentagalloylglucoses has been further studied (compare A., 1915, i, 437), and, through the triacetylgalloyl derivatives, it has now been found possible to isolate products which consist almost entirely of the pentagalloyl derivatives of  $\alpha$ - and  $\beta$ -glucose respectively.

The preparation of 1-galloylglucose,



is also described, this being the first acyl derivative of glucose to which a definite structure can be with certainty assigned. It is in all respects identical with the glucogallin isolated by Gilson from Chinese rhubarb (A., 1903, i, 355).

*Penta-acetyl-m-digalloyl* [*penta-acetoxy-m-benzoyloxybenzoyl*] chloride,  $\text{C}_6\text{H}_3(\text{OAc})_3 \cdot \text{CO} \cdot \text{O} \cdot \text{C}_6\text{H}_3(\text{OAc})_2 \cdot \text{COCl}$ , six-sided plates, m. p. 180° (corr.), after slight previous softening, is obtained by the action of phosphorus pentachloride on *m*-digallic acid in the presence of chloroform, and is converted by methyl alcohol in the presence of quinoline into methyl penta-acetyl-*m*-digallate, m. p. 167—168° (corr.) (compare A., 1918, i, 174). It reacts with  $\beta$ -glucose to yield *penta-(penta-acetyl-m-digalloyl)- $\beta$ -glucose*,



two specimens of which had  $[\alpha]_D^{25} + 3.79^\circ$  and  $[\alpha]_D^{25} + 2.60^\circ$  in *s*-tetrachloroethane. [*Penta-(penta-acetyl-p-digalloyl)- $\beta$ -glucose* is obtained in a similar manner; it has  $[\alpha]_D^{25} + 1.54^\circ$  (in *s*-tetrachloroethane), and resembles the *m*-derivative so closely that an analytical distinction is almost impossible.] *Penta-(m-digalloyl)- $\beta$ -glucose* is prepared by deacetylation of the acetyl derivative with cold aqueous sodium hydroxide at 0°, and is purified by means of the potassium salt; according to the method of separation, it forms

a pale brown, light, amorphous powder, or a compact, honey-yellow, brittle mass. When hydrolysed by dilute sulphuric acid, it gives approximately the same amount of dextrose and gallic acid as does Chinese tannin. When treated with diazomethane, it yields penta-(pentamethyldigalloyl)-glucose, which, like the earlier preparations, is not perfectly uniform, but which shows a very close analogy with the methyl derivative of the natural Chinese tannin. Reacetylation of penta-(*m*-digalloyl)- $\beta$ -glucose shows that a certain amount of change (possibly isomerisation of the  $\beta$ -glucose to  $\alpha$ -glucose derivative) occurs either during hydrolysis or on treatment with acetic anhydride.

*Penta-(penta-acetyl-m-digalloyl)- $\alpha$ -glucose* is prepared in the same manner as the  $\beta$ -derivative; individual preparations had  $[\alpha]_D + 30.8^\circ$ ,  $+ 27.7^\circ$ , and  $+ 25.5^\circ$  (in *s*-tetrachloroethane), pointing to admixture with varying amounts of the  $\beta$ -isomeride. [The corresponding *penta-(penta-acetyl-p-digalloyl)- $\alpha$ -glucose* shows the closest analogy with the  $\beta$ -compound] *Penta-(m-digalloyl)- $\alpha$ -glucose* is a pale brown, amorphous powder which can only be distinguished from the  $\beta$ -glucose derivative by its specific rotation; it has  $[\alpha]_D^{25} + 43.8^\circ$  (in water),  $[\alpha]_D^{25} + 35.8^\circ$  (in alcohol), and  $[\alpha]_D^{25} + 40.1^\circ$  (in acetone).

Acetylation of Chinese tannin yields a penta-(penta-acetyldigalloyl)-glucose closely similar to penta-(penta-acetyl-*m*-digalloyl)- $\beta$ -glucose; the regenerated tannin, however, is found to differ somewhat from the original specimen.

*Penta-(triacylgalloyl)- $\alpha$ -glucose*,  $[C_6H_7(OAc)_3CO]_5C_6H_7O_6$ , is prepared in the usual manner from  $\alpha$ -glucose and triacylgalloyl chloride; it forms an amorphous mass, having  $[\alpha]_D + 42.7^\circ$  to  $+ 46.95^\circ$  in *s*-tetrachloroethane. Deacetylation is accomplished by means of sodium acetate in aqueous acetone solution; the penta-galloyl- $\alpha$ -glucose thus obtained is distinguished from the previous preparation (by hydrolysis of penta-[trimethylcarbonatogalloyl]- $\alpha$ -glucose by alkali) by a considerably higher specific rotation in aqueous and alcoholic solution, but otherwise the resemblance is very close. On treatment with acetic anhydride, the original acetyl derivative is regenerated. Diazomethane converts it into penta-(trimethylgalloyl)- $\alpha$ -glucose, identical with that previously described (*loc. cit.*).

*Penta-(triacylgalloyl)- $\beta$ -glucose* is a pale yellow, amorphous mass which has  $[\alpha]_D^{25} + 5.61^\circ$  or  $+ 4.1^\circ$  in *s*-tetrachloroethane; when deacetylated, it yields penta-galloyl- $\beta$ -glucose, having  $[\alpha]_D^{25} + 23.3^\circ$  (in alcohol),  $[\alpha]_D^{25} + 15.6^\circ$  and  $+ 13.1^\circ$  in 10% and 1% aqueous solution. When treated with diazomethane, it gives a penta-(trimethylgalloyl)- $\beta$ -glucose which, in its properties and optical activity, closely resembles the preparation previously described (A., 1915, i, 438), but which, unlike the latter, could not be caused to crystallise. Reacetylation yields a product closely resembling the original substance. Hydrolysis of the two penta-(triacylgalloyl)-glucoses by alkali at  $0^\circ$  yields  $\alpha$ - and  $\beta$ -derivatives respectively, which are quite distinct, although less so than when

sodium acetate is used. (In the case of the corresponding methylcarbonato-compounds, practically identical products were obtained when the hydrolysis was effected by alkali at the ordinary temperature.)

*Penta-(p-acetoxybenzoyl)- $\alpha$ -glucose*,  $[\text{C}_6\text{H}_4(\text{OAc})\cdot\text{CO}]_5\text{C}_6\text{H}_7\text{O}_6$ , forms fine needles, m. p. 158—159° (corr.),  $[\alpha]_D^{25} + 124.7^\circ$  in *s*-tetrachloroethane; during the preparation, considerable quantities of the  $\beta$ -isomeride are formed, which are removed during purification. The corresponding penta-(*p*-hydroxybenzoyl)- $\alpha$ -glucose could not be caused to crystallise, but the specific rotation of the product (+163.4° in alcohol) was considerably greater than that previously found; on reacylation, it yielded the crystalline acetyl derivative in excellent yield. The preparation of *penta-(p-acetoxybenzoyl)- $\beta$ -glucose* and of *penta-(p-hydroxybenzoyl)- $\beta$ -glucose* is also described, but the substances could not be caused to crystallise, and are probably admixed with the corresponding  $\alpha$ -derivatives.

*Triacetylalloyl-2:3:5:6-tetra-acetylglucose* is prepared from acetobromoglucose and silver triacetylallate; it forms microscopic needles or four-sided leaflets, m. p. 125—126° (corr.), after slight softening,  $[\alpha]_D^{25} - 24.4^\circ$  in *s*-tetrachloroethane. It may also be obtained from tetra-acetylglucose and triacetylalloyl chloride. When dissolved in alcohol and treated with ammonia at 20°, it yields 1-monoalloyl- $\beta$ -glucose, microscopic, oblique prisms or platelets, m. p. 214—215° (corr.; decomp.), when rapidly heated, 202—203° (corr.; decomp.) when slowly heated; it has  $[\alpha]_D^{25} - 25.6^\circ$  in aqueous solution. The product is quite distinct from the glucogallic acid described by Feist (A., 1912, i, 566, 888; 1913, i, 70). When reacylated, it yields triacetylalloyltetra-acetylglucose. Its action towards enzymes has been investigated. Its identity with glucogallin is established both by chemical tests and by measurement of the crystals. *1-Galloyl- $\beta$ -glucosemonoacetate* forms colourless needles,  $[\alpha]_D^{25} + 10.5^\circ$  (in alcohol); it has no distinct m. p., but, when rapidly heated, is converted into a viscous, turbid liquid at about 150° after marked softening. *1-Galloyl- $\beta$ -glucosetetra-acetate* (?) crystallises in needles, m. p. about 136—137°,  $[\alpha]_D^{25} + 38.7^\circ$  (in alcohol), but its isolation in the pure condition is not claimed.

*1-Benzoyltetra-acetylglucose* is prepared from benzoyl chloride and 2:3:5:6-tetra-acetylglucose, and agrees in its properties with the product described by Zemplén and László (A., 1915, i, 651) except in specific rotation ( $[\alpha]_D^{25} - 26.6^\circ$  in chloroform). *1-o-Acetoxybenzoyl-2:3:5:6-tetra-acetylglucose* crystallises in microscopic, flat prisms. It has m. p. 116—117° (corr.),  $[\alpha]_D^{25} - 41.0^\circ$  in *s*-tetrachloroethane.

H. W.

**Structure of  $\beta$ -Glucosidogallic Acid.** EMIL FISCHER and MAX BERGMANN (*Ber.*, 1918, 51, 1804—1808).—The work of Fischer and Strauss (A., 1913, i, 180) has led to the supposition that  $\beta$ -glucosidogallic acid contains the sugar residue attached to the *p*-hydroxyl group of gallic acid; this hypothesis is confirmed by its conversion into glucosyringic acid (Mauthner, A., 1910, i, 667).



Ethyl tetra-acetylglucosidogallate is converted by diazomethane into ethyl tetra-acetylglucosyringate, from which glucosyringic acid is obtained by hydrolysis with barium hydroxide; the free acid has m. p. about  $225^{\circ}$  (decomp.) when moderately rapidly heated and  $[\alpha]_D^{25} - 18.18^{\circ}$  (as sodium salt) in water.

Ethyl triacetyl-gallate has m. p.  $138-139^{\circ}$  (corr.) instead of  $132-134^{\circ}$  (A., 1915, i, 683).

Ethyl hexa-acetylglucosidogallate has m. p.  $176-177^{\circ}$  (corr.),  $[\alpha]_D^{25} - 19.0^{\circ}$  in tetrachloroethane solution. H. W.

**Digitalis Substances. XXXVIII.** H. KILIANI (Ber., 1918, 51, 1613—1639. Compare A., 1916, i, 493).—The preliminary crystallisation from 85% alcohol is unnecessary in order to separate the digitonin from the gitonin in "crude digitonin amylate" (Ber., 1916, 49, 701). It suffices to dissolve the crude amylate in ten parts of boiling 50% alcohol; on cooling, gitonin material separates first and pure digitonin subsequently.

A sample of "soluble digitonin" supplied by Merck proved to be identical with a new glucoside obtained from the final mother liquor of the crude digitonin (*loc. cit.*).

The sugar syrup previously obtained (*loc. cit.*) could not be made to crystallise, because the sugars in the syrup, which had been produced in an alcoholic medium, are present chiefly in the form of ethyl glucosides. After a second hydrolysis with hydrochloric acid, a partial crystallisation can be effected, and *d*-galactose obtained by inoculation; dextrose, identified as *d*-gluconic acid, is present, and apparently also a third sugar, a ketose, since the syrup is shown to contain oxalic and glycollic acids. (The hydrochloric acid was removed by silver oxide, and it is known that silver oxide acts on hexoses, particularly keto-hexoses, to produce these two acids.)

During the conversion of digitogenin,  $C_{31}H_{50}O_6$ , into digitogenic acid,  $C_{28}H_{44}O_8$ , three atoms of carbon are removed. Their fate has not been ascertained; it is shown that they do not appear as acetone, acetaldehyde, malonic, propionic, or carbonic acid.

Digitogenic acid has  $[\alpha]_D - 67.1^{\circ}$  in aqueous potassium hydroxide, and forms a *magnesium* salt,  $C_{28}H_{42}O_8Mg \cdot 7H_2O$ , small, hard nodules of minute needles.  $\beta$ -Digitogenic acid has  $[\alpha]_D - 60.2^{\circ}$  in aqueous potassium hydroxide, and forms a *magnesium* salt, microscopic prisms and needles with  $7H_2O$ . The m. p. of digitogenic acid is altered by crystallisation, and is therefore no safe criterion for identification. The acid is not reduced by hydrogen and colloidal palladium, amalgamated zinc and hydrochloric acid, or zinc dust and acetic acid.

The acid,  $C_{16}H_{24}O_7$ , obtained by the oxidation of digitogenic acid in about 15% yield (*loc. cit.*), is obtained in about 27% yield by oxidising the amorphous precipitate thrown down by adding water to the mother liquor of the crude digitogenic acid. It is oxidised by potassium permanganate in strongly alkaline solution,

yielding an amorphous acid,  $C_{15}H_{22}O_7 \cdot H_2O$ , decomp.  $120-130^\circ$ , softening at about  $70^\circ$ , which forms an amorphous magnesium salt,  $(C_{15}H_{19}O_7)_2 \cdot Mg_3 \cdot 5H_2O$ .

The mother liquor of the crude acid,  $C_{16}H_{24}O_7$  (*loc. cit.*), contains, in addition to other substances, at least two very easily soluble acids, one of which has been identified as ethylsuccinic acid.

The oxidation of gitogenic acid by hot chromic, acetic, and sulphuric acids yields an acid,  $C_{18}H_{26}O_8$ , tufts of needles, m. p.  $210^\circ$ , sintering at about  $206^\circ$  (calcium salt,  $C_{18}H_{26}O_8Ca \cdot 2H_2O$ ), an acid,  $C_{19}H_{30}O_8$ , m. p.  $201-202^\circ$  (calcium salt,  $C_{19}H_{28}O_8Ca$ , amorphous), and ethylsuccinic acid.

Digitoxigenin is not reduced by hydrogen and colloidal palladium, and is oxidised by chromic and acetic acids, yielding a neutral substance,  $C_{18}H_{26}O_4$ , crystals, m. p.  $185^\circ$ .

Digitaligenin forms an acetyl derivative,  $C_{22}H_{32}O_3Ac$ , colourless prisms or needles, m. p.  $201-202^\circ$  (digitaligenin also has m. p.  $201-202^\circ$ , not  $210-212^\circ$ , as stated previously), and is reduced in aqueous methyl-alcoholic solution by hydrogen and colloidal palladium, yielding a substance,  $C_{19}H_{28(101.30)}O_3 \cdot H_2O$ , crystals, m. p.  $182-184^\circ$ , sintering at  $175^\circ$ , which is oxidised by chromic and acetic acids, yielding a neutral substance,  $C_{19}H_{28(101.29)}O_3$ , stout crystals, m. p.  $190-192^\circ$ , and an acid,  $C_{14}H_{20}O_4$  (by analysis) or  $C_{14}H_{18}O_3$  (by titration and by analysis of the calcium salt), colourless prisms sintering at  $240-245^\circ$  without melting. C. S.

### The Isomeric Lactones, Caryophyllin and Urson.

FRANCIS D. DODGE (*J. Amer. Chem. Soc.*, 1918, **40**, 1917-1939).—Comparison of caryophyllin and urson shows a very close similarity of these compounds; in strictly chemical properties no differences have been observed, but the variations in the physical properties appear to warrant the conclusion that they are isomerides of very similar structure. The balance of evidence is in favour of a lactonic constitution, but in certain respects (practically instantaneous neutralisation of alkali in alcoholic solution, opening of lactone ring on acetylation) an unusual behaviour is exhibited.

Caryophyllin is most readily obtained in the pure state through the potassium salt, and crystallises in white needles ( $+2H_2O$ ); the anhydrous substance has m. p. about  $310^\circ$  (corr.),  $[\alpha]_D^{25} + 54.5^\circ$  in alcoholic solution; in a vacuum tube at  $280-300^\circ$  it sublimes in characteristic rosettes. The potassium salt forms well-defined prisms ( $+1.5H_2O$ ); the anhydrous salt has  $[\alpha]_D^{25} + 63.4^\circ$  in ethyl alcohol,  $[\alpha]_D^{25} + 67.7^\circ$  in methyl alcohol. Analyses lead to the formula  $C_{30}H_{48}O_4K$  for the salt, and hence to  $(C_{10}H_{16}O)_3$  for caryophyllin. The calcium, lead, magnesium, zinc, and silver salts are described.

Acetylation of caryophyllin under various conditions leads to the formation of diacetylcaryophyllinic acid and acetylcaryophyllin; the former substance is somewhat unstable, but can be obtained in the pure state by evaporation of an ethereal solution of the crude acetylation product at the ordinary temperature. It slowly loses acetic acid at the ordinary temperature, and is converted into

acetylcaryophyllin by boiling ethyl alcohol or glacial acetic acid. The *potassium* salt is described. Acetylcaryophyllin forms white, efflorescent needles, m. p. 260—265°, and yields a *potassium* salt which is readily soluble in alcohol. A very sparingly soluble substance, possibly a polymeric acetate, is also obtained during the acetylation of caryophyllin.

Oxidation of caryophyllin with fuming nitric acid yields caryophyllic acid, which is shown to be a somewhat unstable, tribasic acid,  $C_{27}H_{45}O_5(CO_2H)_3$ , giving a characteristic, sparingly soluble, mono-*potassium* salt. When heated with acetic anhydride it yields a compound, m. p. 210—213° (slight decomp.), which appears to be an acetyl dilactone,  $C_{31}H_{46}O_6$ , a molecule of carbon dioxide being eliminated during the process.

Urson in its general properties is very similar to caryophyllin. The most striking difference is shown by the potassium salts, that derived from urson being freely soluble in ethyl alcohol, in which the caryophyllin salt is sparingly soluble; a method of separation is based on this dissimilarity. The *lead*, *zinc*, *magnesium*, and *ammonium* (?) salts of urson are described. Urson diacetate (diacetylursonic acid) closely resembles the corresponding derivative of caryophyllin, but is, in general, more soluble and less stable. Decomposition to the mono-acetate occurs so readily that it was found impossible to prepare a pure compound. Acetylurson separates from alcohol in plates or prisms ( $+5H_2O$ ) quite different in appearance from the caryophyllin compound. It was not found possible to purify the product formed by the oxidation of urson with fuming nitric acid. H. W.

**4-Phenylcoumarins. II.** ADOLF SONN (*Ber.*, 1918, 51, 1829—1832. Compare A., 1918, i, 401).—Further examples of the formation of 4-phenylcoumarins are given.

Chloroacetylresorcinol dimethyl ether, m. p. 114—115° after softening at 112° [Tamber and du Bois (A., 1918, i, 395) give 119°], is obtained by the action of hydrogen chloride on an ethereal solution of resorcinol dimethyl ether and chloroacetonitrile in the presence of zinc chloride, and is converted by potassium cyanide into *cyanoacetylresorcinol dimethyl ether*, prisms or plates, m. p. 152—153°. The latter condenses with phloroglucinol in glacial acetic acid solution under the influence of zinc chloride and hydrogen chloride, yielding 5:7-*dihydroxy*-2':4'-*dimethoxy*-4-*phenylcoumarin*, hexagonal prisms, m. p. 232° (decomp.).

Similarly, *cyanoacetylcatechol*, m. p. 222° (decomp.), after previous softening, condenses with phloroglucinol to 3':4':5:7-*tetrahydroxy*-4-*phenylcoumarin*, which, after being purified through the acetyl derivative, forms platelets ( $+2H_2O$ ), m. p. about 270° (decomp.). H. W.

**Improvements in and Relating to Synthetic Drugs [Mydriatic Alkaloids].** NAGAYOSHI NAGAI (*Brit. Pat.* 120936).

—Synthetic racemic *N*-methylmydriatine,



or its salts is prepared by the condensation of benzaldehyde with nitroethane by agitation for several hours at the ordinary temperature in the presence of a small quantity of a solution of a weak alkali, such as an alkali carbonate or hydrogen carbonate, or phosphate, or pyridine, etc. The condensation product, phenylnitropropanol,  $\text{OH}\cdot\text{CHPh}\cdot\text{CHMe}\cdot\text{NO}_2$ , is separated by extraction with ether and freed from benzaldehyde by shaking the ethereal solution with aqueous sodium hydrogen sulphite. The oily residue is dissolved in dilute alcohol, the calculated quantity of formaldehyde is added, and the mixture is reduced at a low temperature by adding dilute acetic acid and zinc dust. The liquid is filtered and the zinc precipitated by hydrogen sulphide; the solution is evaporated in a vacuum and the resinous residue is shaken with dilute hydrochloric acid and ether. The hydrochloride of the base is obtained by evaporating the aqueous layer, and is recrystallised from absolute alcohol. This synthetic ephedrine differs in constitution from Fournieu's ephedrine (A., 1907, i, 762), and is the racemic form of natural ephedrine.

J. F. B.

**Alkaloids of the Betel Nut.** KARL FREUDENBERG (*Ber.*, 1918, 51, 1668—1682).—Guvacine is 1:2:5:6-tetrahydropyridine-3-carboxylic acid according to the author (A., 1918, i, 403) and 1:2:5:6-tetrahydropyridine-4-carboxylic acid according to Hess and Leibbrandt (A., 1918, i, 401). The author now shows that his view is the correct one by (i) the direct comparison (mixed m. p.'s, etc.) of corresponding derivatives of guvacine and Wohl and Johnson's 1:2:5:6-tetrahydropyridine-3-carboxylic acid, (2) by the identity of *N*-methylguvacine with natural arecaine, and (3) by a comparison of dihydroguvacine with nipecotinic acid and *isonipecotinic* acid. Contrary to the statement of Hess and Leibbrandt, dihydroguvacine differs in every way from *isonipecotinic* acid, and is completely identical with nipecotinic acid (piperidine-3-carboxylic acid). Dihydroguvacine has m. p. 261° (decomp.; corr.), not above 320°, as stated by Hess and Leibbrandt (*loc. cit.*). The nipecotinic acid used by Hess and Leibbrandt was in reality almost pure *isonipecotinic* acid. Several other errors in their paper are corrected; for example, *N*-methylguvacine (arecaine, arecaine), when esterified by alcoholic hydrogen chloride, is not demethylated at the nitrogen atom.

C. S.

**The Physical Constants of Nicotine. I. Specific Rotatory Power of Nicotine in Aqueous Solution.** HARRY JEPHCOTT (T., 1919, 115, 104—108).

**Some Derivatives of Pyrrole. IV.** G. KARL ALMSTRÖM (*Annalen*, 1918, 416, 279—290. Compare A., 1913, i, 1240; 1915, i, 989; 1916, i, 568).—In some reactions 5-hydroxy-4-acetyl-1:3-diphenylpyrrole (A., 1916, i, 568) behaves as though it were the 5-keto-compound. It is not attacked by boiling alkali hydroxide and benzaldehyde, but by heating with methyl iodide and alcoholic sodium methoxide at 100° yields a mixture of 4-acetyl-1:3-diphenyl-4-

VOL. CXVI. i.

*methyl-5-pyrrolone*, colourless crystals, m. p. 115—116° (*semicarbazone*, m. p. 217° [decomp.]), and 1:3-diphenyl-4-methyl-5-pyrrolone, colourless needles, m. p. 113—114°. The latter of these is also obtained by heating the former with moderately concentrated sulphuric acid, and is oxidised by chromic and acetic acids to phenyl.

*methylmaleinphenylimide*,  $\begin{matrix} \text{CMe}\cdot\text{CO} \\ | \\ \text{CPh}\cdot\text{CO} \end{matrix} > \text{NPh}$ , pale yellow, quadratic plates, m. p. 106—107°, from which aniline and *phenylmethylmaleic anhydride*, m. p. 94—95°, are obtained by boiling with alcoholic sodium ethoxide.

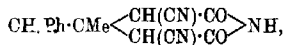
By heating on the water-bath with 2*N*-sodium hydroxide and a large excess of methyl sulphate, 5-hydroxy-4-acetyl-1:3-diphenylpyrrole yields 1:3-diphenyl-4-methyl-5-pyrrolone and 4-acetyl-5-methoxy-1:3-diphenylpyrrole, colourless crystals, m. p. 101°, which forms a *semicarbazone*, pale yellow crystals, m. p. 215° (decomp.), yields 1:3-diphenyl-5-pyrrolone by heating with moderately concentrated sulphuric acid, and is converted into 4-cinnamoyl-5-methoxy-1:3-diphenylpyrrole, yellow crystals, m. p. 111—112°, by heating with aqueous-alcoholic sodium hydroxide and benzaldehyde.

1:3-Diphenyl-4-ethyl-5-pyrrolone, colourless plates, m. p. 118—119°, yields *phenylethylmaleinphenylimide*, yellow, rhombic plates, m. p. 79—80°, by oxidation, from which aniline and *phenylethylmaleic anhydride*, m. p. 46°, are obtained by the action of sodium ethoxide.

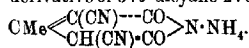
5-Hydroxy-4-acetyl-1:3-diphenylpyrrole does not yield crystalline products by treatment with acetic anhydride, diazomethane, or acetyl chloride, but it reacts with magnesium methyl iodide and then with acetyl chloride to form a substance,  $\text{C}_{18}\text{H}_{15}\text{O}_3\text{N}$ , colourless needles, m. p. 119—120°. C. S.

**General Reaction of Ketones.** I. GUARESCHI (*Gazzetta*, 1918, 48, ii, 83—98).—The author has extended his work on the condensation of ketones with ethyl cyanoacetate in presence of ammonia or an amine (A., 1902, i, 819) to benzyl methyl ketone and its homologues in order to ascertain which ketones react incompletely or not at all with the cyanoacetate, and to study the manner in which the new compounds decompose with formation of hydrocarbons.

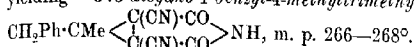
3:5-Dicyano-2:6-diketo-4-benzyl-4-methylpiperidine,



the 1-ammonium derivative of which is formed from benzyl methyl ketone, ethyl cyanoacetate, and ammonia, crystallises in shining needles or prisms, m. p. 255—257°, and has an acid reaction in aqueous solution; its ammonium salt is crystalline, and in aqueous solution decomposes with difficulty into toluene and the ammonium derivative of 3:5-dicyano-2:6-diketo-4-methyl-Δ<sup>3</sup>-tetrahydropyridine.

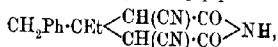


With bromine water 3:5-dicyano-2:6-diketo-4-benzyl-4-methyl-piperidine gives a dibromo-derivative, which, when boiled with alcohol, best with addition of a little formic acid, rapidly loses bromine, yielding 3:5-dicyano-4-benzyl-4-methyltrimethylenedicarbonimide,

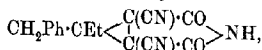


$\beta$ -Phenylethyl methyl ketone yields 3:5-dicyano-2:6-diketo-4- $\beta$ -phenylethyl-4-methylpiperidine, which has been already described.

3:5-Dicyano-2:6-diketo-4-benzyl-4-ethylpiperidine,

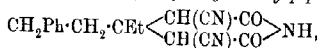


obtained from benzyl ethyl ketone, forms crystals, m. p.  $232-236^\circ$ , which absorb bromine, giving the dibromo-derivative. The latter loses its bromine when boiled with alcohol and formic acid, yielding 3:5-dicyano-4-benzyl-4-methyltrimethylenedicarbonimide,



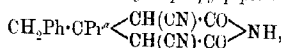
m. p.  $226-228^\circ$ .

3:5-Dicyano-2:6-diketo-4- $\beta$ -phenylethyl-4-ethylpiperidine,



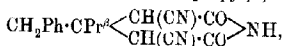
prepared from  $\beta$ -phenylethyl ethyl ketone, forms crystals, m. p.  $181-183^\circ$ .

3:5-Dicyano-2:6-diketo-4-benzyl-4-propylpiperidine,



forms white crystals, m. p.  $225^\circ$ .

3:5-Dicyano-2:6-diketo-4-benzyl-4-isopropylpiperidine,



forms colourless needles, m. p.  $248.5-249.5^\circ$ . When treated with alcohol and formic acid, its dibromo-derivative decomposes, yielding a colourless, crystalline compound, m. p.  $255-257^\circ$ , which is probably 3:5-dicyano-4-benzyl-4-isopropyltrimethylenedicarbonimide.

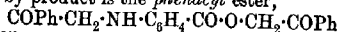
Benzyl isobutyl ketone condenses with ethyl cyanoacetate and ammonia, giving a small quantity of a compound which crystallises in needles, m. p.  $223-225^\circ$ , but was not analysed.

With sodium hydrogen sulphite, benzyl methyl ketone,  $\beta$ -phenylethyl methyl ketone, and benzyl ethyl ketone form crystalline compounds, but this is apparently not the case with  $\beta$ -phenylethyl ethyl ketone or benzyl isobutyl ketone.

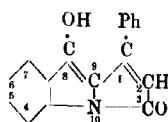
T. H. P.

**The Three Phenacylaminobenzoic Acids.** M. SCHOLTZ (*Ber.*, 1918, **51**, 1645-1653).—The three aminobenzoic acids react with *o*-bromoacetophenone in boiling alcohol to form *o*-phenacylaminobenzoic acid,  $\text{COPh}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , yellow leaflets, m. p.  $190^\circ$  (phenylhydrazone, yellow needles, m. p.  $156^\circ$ ), the *m*-isomeride,

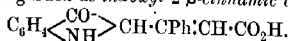
colourless crystals, m. p. 202°, and the *p*-isomeride, colourless needles, m. p. 211° respectively. If alkali hydroxide or carbonate also is present in the reaction in the case of the ortho- and para-compounds, a by-product is the *phenacyl* ester,



(*o*-ester, hair-like crystals, m. p. 180°; *p*-ester, colourless needles, m. p. 186°). By treatment with boiling acetic anhydride *m*- and *p*-phenacylaminobenzoic acids are converted into the corresponding *N*-acetyl derivatives, pointed prisms, m. p. 217°, and leaflets, m. p. 176°, respectively, but the ortho-compound is converted into a sub-



stance,  $\text{C}_{17}\text{H}_{11}\text{O}_2\text{N}$ , colourless needles, m. p. 288°, which is regarded as 8-hydroxy-3-phenyl-1-phenylpropenylidene-2:1-indole (annexed formula). It develops a blood-red coloration with alcoholic ferric chloride, forms a dibromide,  $\text{C}_{17}\text{H}_{11}\text{O}_2\text{NBr}_2$ , pale yellow needles, m. p. 265°, and is converted by hot aqueous alcoholic potassium hydroxide into the potassium salt of an acid,  $\text{C}_{17}\text{H}_{13}\text{O}_3\text{N}$ , colourless needles, m. p. 300° (decomp.), which does not give a coloration with ferric chloride, forms a dibromide, pale yellow needles, and yields a phenylhydrazone, yellow needles, m. p. 221°, and is therefore regarded as indoxyl-2- $\beta$ -cinnamic acid,



It is acetylated by warming with acetic anhydride, but the product,  $\text{C}_{17}\text{H}_{12}\text{O}_3\text{NAc}$ , rhombic crystals, m. p. 167°, no longer exhibits the properties of an acid; it regenerates indoxylcinnamic acid after prolonged boiling with aqueous sodium hydroxide.

By boiling with phenylhydrazine in glacial acetic acid all three phenacylaminobenzoic acids yield the phenylhydrazone of *s*-phenacylphenylhydrazine,  $\text{NHPh} \cdot \text{N} \cdot \text{CPh} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{NHPh}$ , yellow needles, m. p. 147° (acetyl derivative,  $\text{C}_{20}\text{H}_{19}\text{N}_4\text{Ac}$ , yellow crystals, m. p. 201°).

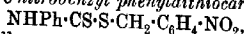
$\omega$ -Bromoacetophenone and phenylhydrazine react in boiling alcohol to form, not the preceding compound, but a substance,  $\text{C}_{28}\text{H}_{24}\text{N}_4$ , colourless needles, m. p. 174°, which is regarded as tetra-

phenyl- $\beta$ -tetracarbazone,  $\text{CPh} \cdot \text{CH}_2 \cdot \text{NPh} \cdot \text{N} \cdot \text{NPh} \cdot \text{CH}_2 \cdot \text{CPh}$ , and is isomeric with the substance, m. p. 137°, obtained by Hess in 1886 from the same two reagents in alcoholic solution at 0°. C. S.

**Aldehyde Derivatives of Rhodanines and their Fission Products. I.** RUDOLF ANDREASCH (*Monatsh.*, 1918, **39**, 419–440).—A study of the oxidation, reduction, and fission of various condensation products of aldehydes and rhodanines.

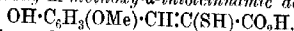
A solution of phenylbenzylidenerhodanine in boiling glacial acetic acid is oxidised by bromine to phenylbenzylidenethiocarbimideglycolide, m. p. 209° (compare A., 1917, i, 663, in which the m. p. is given as 239° in error); similarly, phenyl-*o*-nitrobenzylidenerhodanine yields phenyl-*o*-nitrobenzylidenethiocarbimideglycolide, woolly needles, m. p. 204°.

The following substances have been prepared with a view to the study of their reduction: 5-ethylrhodanine (from ethyl  $\alpha$ -bromobutyrate and ammonium dithiocarbamate), yellowish-white, crystalline powder, m. p. 105°; 3-phenyl-5-ethylidenerhodanine, thin, pale yellow plates, m. p. 123°; 3-phenyl-5-ethylrhodanine, pale yellow needles, m. p. 83°; *o*-nitrobenzyl phenyldithiocarbamate,

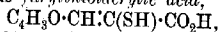


sulphur-yellow needles, m. p. 120—121°. Attempts to reduce ethylidenerhodanine and phenylethylidenerhodanine have not yielded satisfactory results up to the present.

The various aldehyde condensation products of the rhodanines are found to be decomposed with widely differing velocities by alkali; those containing a hydroxy-group in the phenyl residue are particularly resistant, so that, in general, they are only decomposed under conditions which lead to the further degradation of their fission products. The most suitable reagent is a solution of sodium amyloxide in amyl alcohol, probably by reason of the higher temperature which can be attained. Under these conditions, phenylpiperonylidenerhodanine yields phenylthiocarbimide and methylenedioxy- $\alpha$ -thiolcinnamic acid,  $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}_5 \cdot \text{CH} : \text{C}(\text{SH}) \cdot \text{CO}_2\text{H}$ , yellow, microscopic needles, which begin to decompose at ca. 170° and are completely molten at 208—210°. The latter acid is transformed by iodine into disulphidobismethylenedioxy-cinnamic acid, m. p. 228°. Similarly, *p*-hydroxy-*m*-methoxy- $\alpha$ -thiolcinnamic acid,



pale chrome-yellow, rhombic plates, m. p. 183° after softening at 170°, is obtained from the condensation product of vanillin and phenylrhodanine, whilst the anhydride of *o*-hydroxy- $\alpha$ -thiolcinnamic acid (m. p. of benzyl derivative, 164—165°) is prepared from phenyl-*o*-hydroxybenzylidenethiocarbimideglycollide. Phenylfurylidenerhodanine yields furylthiolacrylic acid,



fine needles, m. p. 102—103°, which is transformed by iodine into the corresponding disulphido-acid, lemon-yellow needles or hexagonal plates, m. p. 190—191°. Fission of *p*-hydroxybenzylidenerhodanine, m. p. 274° after softening at 260°, did not lead to the isolation of *p*-hydroxy- $\alpha$ -thiolcinnamic acid, but its formation was proved by the separation of its benzyl derivative, colourless, microscopic needles, m. p. 183°. The free acid, chrome-yellow needles, m. p. 186°, was prepared by the action of a solution of sodium amyl oxide in hot amyl alcohol on phenyl-*p*-hydroxybenzylidenerhodanine, cadmium-yellow needles, m. p. 285°. The corresponding disulphido-acid is a yellow, crystalline powder, m. p. 197°. *p*-Dimethylaminomethylthiolcinnamic acid has m. p. 160°; the corresponding disulphido-acid is a scarlet powder, m. p. 198°.

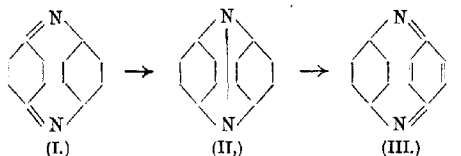
*p*-Aminobenzylidenerhodanine forms fine, woolly needles resembling chromium trioxide which soften at about 200°, and are not completely melted at 290°; 2:4-diketo-5-*p*-aminobenzylidenethiazoline,  $\begin{matrix} \text{CO} \rightarrow \text{S} \\ \text{NH} \cdot \text{CO} \end{matrix} > \text{C} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ , is a dark reddish-brown powder



which further darkens from about 200°, and has no definite m. p. Attempts to decompose these substances, as also phenyl-*o*-nitrobenzylidenerhodanine, by alkali led to negative results. H. W.

**Parabanic Acid.** ROBERT BEHREND and ADOLF ASCHÉ (*Annalen*, 1918, **416**, 226—228).—Parabanic acid can be obtained in about 33% yield by rapidly adding 8.4 grams of uric acid to 39 c.c. of nitric acid, D 1.3, heated at 70°, evaporating the solution to dryness, and evaporating the residue two or three times with nitric acid, D 1.4, until the evolution of gas ceases. The product is crystallised from boiling water. C. S.

**New Compounds to be employed as Colouring Matters or in the Production of Colouring Matters.** ANDREA ANGEL (*Eng. Pat.*, 121347, 1917).—A new type of compounds, for which the name of "parazenes" is suggested, contains two benzene nuclei (or nuclei of benzene derivatives or other cyclic groups) linked together through four para-carbon atoms of the nuclei by two nitrogen atoms. Of the three phases of the formula which may be assigned to parazene, two (I and III) become identical in the absence of unsymmetrical substitution:



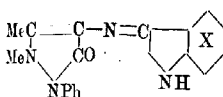
Parazenes are prepared by heating a parahalogen substituted aniline or  $\alpha$ -naphthylamine, or derivatives of either containing indifferent groups in the nuclei, with a condensing agent, such as zinc chloride, ferric chloride, aluminium chloride, or phosphoric oxide. The product of the reaction is a hydroxyparazene, which is converted by reduction into parazene. The parazene thus obtained from *p*-chloroaniline is a dark blue powder which, when dissolved in dilute acetic acid, may be used for dyeing wool or silk. Special colouring matters may be produced by introducing auxochromic groups by the ordinary methods. Parazenes will form salts with acids by addition to one or both of the nitrogen atoms. [See, further, *J. Soc. Chem. Ind.*, 1919, February.] C. A. M.

**Interaction of Aliphatic Diazo-compounds and Diphenylketen.** J. SUREDA Y BLANES (*Anal. Fis. Quim.*, 1918, **16**, 611—624).—With phenyldiazomethane, diphenylketen produces a substance,  $C_{21}H_{16}ON_2$ , white crystals, m. p. 196°. Diphenyldiazomethane and diphenylketen yield yellow crystals, m. p. 133—135° (decomp.). The product from diphenylenediazomethane and diphenylketen is a dark yellow powder, m. p. 157° (decomp.). The constitution of these substances is being further investigated. A. J. W.

**Preparation of True Vat Dyes from Di- and Tri-aryl-methane Dyes.** HEINRICH WIELAND (D.R.-P. 308298; from *Chem. Zentr.*, 1918, ii, 782—783).—By treatment of the dyes with alkali hyposulphite solution, colourless alkali salts are obtained which are soluble in water, and are reoxidised to the original dyes with extraordinary rapidity by atmospheric oxygen. For example, crystal violet yields sodium hexamethyltriaminotriphenylmethanesulphonate,  $C(C_6H_4 \cdot NMe_2)_3 \cdot SO_3Na$ , crystallising in glistening needles.

H. W. B.

**Some Derivatives of Isatin.** ANDRÉ MEYER (*Compt. rend.* 1918, 167, 1070—1073).—When the amino-oxindole obtained by the reduction of isatoxime with tin and hydrochloric acid is oxidised by potassium ferricyanide in dilute solution, in addition to isatin, a small amount of a red compound is obtained. If the isatoxime is reduced by zinc and acetic acid, the zinc salt,  $C_{16}H_{12}O_2N_2Zn$ , of this red compound is obtained. From its behaviour on reduction with sodium hyposulphite or when dissolved in sulphuric acid, the author considers that the red compound is probably identical with

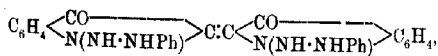


Wahl and Bagard's *isoindigotin*.

Mixed rubazonic acids of the isatin series may be prepared by condensing, in alcoholic solution, amino-antipyrine with isatin, 5-bromoisatin, 5:7-dibromoisatin, and naphthisatin. They have the general constitution (annexed formula), where X represents the substituted benzene or naphthalene nucleus.

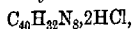
W. G.

**Derivatives of the Indole and Indigotin Groups Substituted at the Nitrogen Atom.** AUGUST ALBERT (*Annalen*, 1918, 416, 240—278. Compare A., 1916, i, 821).—1-Hydroxy-2-thio-3-benzoyloxyoxindole (A., 1915, i, 595) only reacts in the thion form in forming the acetyl derivative. In all other cases, it reacts in the thiol-form,  $C_6H_4 \text{---} \text{CH}(\text{OBz}) \text{---} \text{NO} \text{---} \text{C} \text{---} \text{SH}$ . For example, it reacts with phenylhydrazine in cold alcoholic or glacial acetic acid solution to form 2-thiol-3-benzoyloxyoxindolephenylhydrazone hydrate,  $\text{NHPh} \cdot \text{NH} \cdot \text{N}(\text{OH}) \text{---} \text{CH}(\text{OBz}) \text{---} \text{C}(\text{SH}) \text{---}$ , pale yellow plates, n. p. 123—126° (decomp.), which is also formed from the acetyl derivative, acetic acid being eliminated. The phenylhydrazone hydrate is interesting in that the sulphur can be extraordinarily easily eliminated. *N*/2-Sodium hydroxide converts it into 1:1'-bisphenylhydrazinoindigotin,



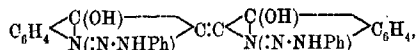
red, rectangular plates, decomp. 237—240°, darkening at 230°, in

which the presence of the two carbonyl groups is shown (1) by heating on the water-bath with aniline or *p*-toluidine and its hydrochloride, whereby the *hydrochloride* of the *anil*,

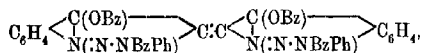


steel-blue needles, decomp.  $240^\circ$ , or of the *p*-tolil, greenish-blue crystals, decomp.  $218\text{--}223^\circ$ , is obtained, and (2) by heating with phenylhydrazine and its hydrochloride, whereby the *bisphenylhydrazone*,  $\text{C}_{40}\text{H}_{34}\text{N}_{10}$ , yellow plates, decomp.  $200\text{--}206^\circ$ , is obtained.

Certain reactions indicate that 1:1'-bisphenylhydrazinoindigotin is able to react in the tautomeric enolic form,



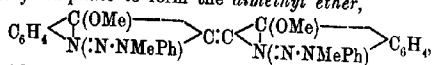
Thus the substance is insoluble in dilute aqueous sodium hydroxide, and is only sparingly soluble in alcohol, but dissolves extremely easily in alcoholic sodium hydroxide, the colour of the solution changing from yellow to blood-red; the yellow colour is regenerated by the addition of water. These colour changes are still more pronounced in the case of the 1:1'-bisphenylmethylhydrazinoindigotin mentioned below; the yellow colour of its alcoholic solution is changed to dark green by alcoholic potassium hydroxide, and is regenerated by the addition of water. The presence of two hydroxyl groups is proved by means of benzoyl chloride. 1:1'-Bisphenylhydrazinoindigotin is boiled with 10*N*. sodium hydroxide until the dark red *sodium* derivative is formed, the mixture is then cooled and treated with benzoyl chloride, whereby, according to the conditions, the *dibenzoyl* derivative,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{N}(\text{NH}\cdot\text{NBzPh}) \end{array} \text{C}:\text{C} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{N}(\text{NH}\cdot\text{NBzPh}) \end{array} \text{C}_6\text{H}_4$ , yellowish-red needles, *m. p.*  $190\text{--}191^\circ$  (this forms a *bisphenylhydrazone*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{C}(\text{N}\cdot\text{NHPh}) \\ \diagup \quad \diagdown \\ \text{N}(\text{NH}\cdot\text{NBzPh}) \end{array} \text{C}:\text{C} \begin{array}{c} \text{C}(\text{N}\cdot\text{NHPh}) \\ \diagup \quad \diagdown \\ \text{N}(\text{NH}\cdot\text{NBzPh}) \end{array} \text{C}_6\text{H}_4$ , pale yellow plates containing  $2\text{H}_2\text{O}$ , *m. p.*  $140\text{--}145^\circ$  [hydrated] or  $186\text{--}189^\circ$  [decomp.; anhydrous]), or the *tetrabenzoyl* derivative,



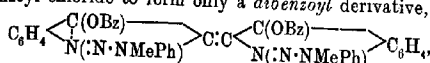
yellow or yellowish-brown, rhombic plates, *m. p.*  $158\text{--}159^\circ$ , is obtained. The *tetrabenzoyl* derivative is converted into the *dibenzoyl* derivative by careful treatment with sodium ethoxide, and into the *bisphenylhydrazone* of the latter by warming with phenylhydrazine and its hydrochloride at  $50^\circ$ .

By treatment with *as*-phenylmethylhydrazine, 1-hydroxy-3-benzoyloxy-2-thio-oxindole is converted into a phenylmethylhydrazone, which could not be obtained crystalline, and is readily changed by *N*/2-sodium hydroxide into 1:1'-bisphenylmethylhydrazinoindigotin,  $\text{C}_{40}\text{H}_{36}\text{O}_2\text{N}_6$ , yellow or yellowish-red needles, *m. p.*  $202^\circ$  (*bisphenylhydrazone*,  $\text{C}_{42}\text{H}_{38}\text{N}_{10}$ , yellowish-brown plates,

decomp. 165°). This reacts with cold alcoholic potassium ethoxide and methyl sulphate to form the *dimethyl ether*,



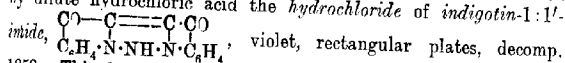
dark bluish-red plates, m. p. 105°, and its *sodium* derivative reacts with benzoyl chloride to form only a *dibenzoyl* derivative,



yellow, quadratic plates, m. p. 150—151°. The dibenzoyl derivative is converted into the preceding bisphenylhydrazone, decomp. 165°, by warming with phenylhydrazine, the two benzoyl groups being eliminated.

1:1'-*Bis-p-bromophenylhydrazinoindigotin*,  $\text{C}_{28}\text{H}_{20}\text{O}_2\text{N}_6\text{Br}_2$ , forms orange-yellow, rectangular plates, m. p. 247° (decomp.), and is converted by warm aniline and aniline hydrochloride into the *hydrochloride* of the *anil*,  $\text{C}_{40}\text{H}_{30}\text{N}_8\text{Br}_2\cdot 2\text{HCl}$ , blackish-blue, microscopic plates, m. p. 227—231° (decomp.).

The preceding bisphenylhydrazino- and substituted bisphenylhydrazino-indigotins do not yield vat dyes on reduction, but undergo profound decomposition, the products depending on the nature of the reducing agent. The course of the reduction in acid media will be described in a later paper. The reduction of 1:1'-bisphenylhydrazinoindigotin suspended in benzene by alcoholic ammonium sulphide yields dihydroindigotin, aniline, and ammonia. Its reduction by *N*-sodium hydroxide and zinc dust in an atmosphere of coal gas for six days yields a pale yellow solution, from which is precipitated by means of atmospheric oxygen a dark blue zinc salt, probably of 1:1'-diaminoindigotin, from which is liberated by dilute hydrochloric acid the *hydrochloride* of *indigotin*-1:1'-



violet, rectangular plates, decomp. 185°. This base forms an *acetyl* derivative, a very sparingly soluble *sulphate*,  $2\text{C}_{16}\text{H}_9\text{O}_2\text{N}_3\cdot\text{H}_2\text{SO}_4$ , needles, and other crystalline salts, and is a true vat dye, yielding with alkaline sodium hyposulphite a yellow vat from which the imide is regenerated by means of oxygen. The preceding zinc salt yields dihydroindigotin by reduction.

C. S.

**Compounds Derived from Proteins by Energetic Treatment with Nitric Acid. VII.** CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1918, 103, 80—83. Compare A., 1918, i, 198).—The occurrence of 5-nitroglyoxaline-4-carboxylic and glyoxaline-4-glyoxylic acids, both oxidation products of histidine, among the products of the oxidation of protein, is confirmed (see Knoop, A., 1918, i, 412).

H. W. B.

**Hydrolysis of Kafirin.** D. BREESE JONES and CARL O. JOHNS (*J. Biol. Chem.*, 1918, 36, 323—334).—Kafirin, the alcohol-soluble protein of kafir (*Andropogon sorghum*), contains 21.2%

glutamic acid, 15.4% leucine, 8.1% alanine, 7.8% proline, 5.5% tyrosine, 4.3% valine, 3.5% ammonia, 2.3% phenylalanine, 2.3% aspartic acid, 1.6% arginine, 1.1% histidine, 0.95% lysine, and 0.84% cystine. Tryptophan is also present, but glycine is absent. Kafirin therefore closely resembles zein, the alcohol-soluble protein of maize, except in regard to its content of tryptophan.

H. W. B.

**Proteins of the Peanut, *Arachis hypogaea*. III. The Hydrolysis of Arachin.** CARL O. JOHNS and D. BREESH JONES (*J. Biol. Chem.*, 1918, **36**, 491–500. Compare preceding abstract).—Arachin contains 16.7% glutamic acid, 13.5% arginine, 5.5% tyrosine, 5.3% aspartic acid, 5.0% lysine, 4.1% alanine, 3.9% leucine, 2.6% phenylalanine, 2.0% ammonia, 1.9% histidine, 1.4% proline, 1.1% valine, and 0.9% cystine. Tryptophan is present, glycine absent.

H. W. B.

**Chemical Study of Enzyme Action.** K. G. FALK (*Science*, 1918, **47**, 423–429; from *Physiol. Abstr.*, 1918, **3**, 407).—The chemical nature of enzymes is discussed in the light of the results of experiments previously published (compare A., 1917, i, 598).

H. W. B.

**Studies in Fermentation. III. Pepsin and Peptic Digestion.** W. BIEDERMANN (*Fermentforsch.*, 1917, **2**, 1–57; from *Chem. Zentr.*, 1918, ii, 741–742. Compare A., 1917, i, 62).—A suspension of coagulated egg white in water can be employed for detecting a small amount of pepsin. The former is prepared from dried commercial egg albumin by dissolving in water, acidifying with acetic acid, adding sodium chloride, and then heating to the boiling point with continual stirring. The protein separates in very finely divided flocks, which after washing and pressing can be rubbed up with a little glycerol to form a paste, in which form it can be preserved indefinitely. A small fragment about the size of a pea in 10 c.c. of water forms a milky fluid which does not yield a perceptible sediment for several hours. On digestion with a trace of pepsin and hydrochloric acid, the turbidity quickly disappears.

Fibrin is dissolved by dilute hydrochloric acid even in the absence of pepsin. Repeated addition of fibrin results in an increased rate of solution, which appears to indicate that an autolytic or peptic enzyme is closely associated with fibrin or is formed from the fibrin by hydrolysis. If the fibrin is boiled prior to the experiment, it does not dissolve so readily in the dilute acid.

H. W. B.

**Trypsin, and a New Method of Purifying Enzymes.** JOSEPH T. WOOD (*J. Soc. Chem. Ind.*, 1918, **37**, 313–315c).—It has been stated by Holzberg (A., 1913, i, 662) that when a saturated solution of safranin is added to a neutral or very faintly alkaline solution of trypsin, a precipitate is formed which possesses proteolytic properties. This statement is confirmed by the author, and it

is shown that the precipitated material consists of protein matter with the safranine and the enzyme in an adsorbed condition.

Trypsin or other enzyme can be purified by dissolving in a small quantity of water and allowing the solution to soak into filter or blotting paper. After rapid drying at a low temperature, the proteins are retained more tenaciously by the paper than the enzyme, and on placing in water for a few minutes and then filtering, a solution of the enzyme is obtained practically free from protein. Such a protein-free trypsin solution does not give any precipitate with safranine.

H. W. B.

**Action of Mercuric Acetate on *p*-Toluidine. I. L. VECCHIOTTI** (*Gazzetta*, 1918, **48**, ii, 78—83. Compare A., 1914, i, 1063).—The interaction of mercuric acetate (1 mol.) and *p*-toluidine (1 mol.) yields *p*-toluidine-mercuriacetate,



which forms shining, white crystals, m. p. 184°; the mercuriacetate group probably occupies the ortho-position to the amino-group. The corresponding *hydroxide*,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\text{Me}\cdot\text{Hg}\cdot\text{OH}$ , crystallises in pale yellow plates, m. p. 212—213°, which begin to turn brown at about 120°; it renders water strongly alkaline. The *chloride*,  $\text{C}_6\text{H}_4\text{NClHg}$ , forms prismatic needles, m. p. 170°.

T. H. P.

## Physiological Chemistry.

**Quantitative Evaporation of Blood Serum.** GEORGE H. BURROWS and EDWIN J. COHN (*J. Biol. Chem.*, 1918, **36**, 587—590).

—The apparatus consists of an ordinary distilling flask of at least 1 litre capacity supplied with 100 grams of rather large glass pearls. The stopper carries a dropping funnel, the lower end of which extends into the bulb of the flask. The side-tube of the flask is connected with a vertical condenser, which empties into a previously weighed bottle of size suitable for trapping the evaporated and condensed water. Following this in succession is a weighed calcium chloride tower, a manometer, and a vacuum pump. The trap bottle and calcium chloride tower are immersed in ice-cold water, and ice-water should flow through the condenser jacket.

The flask and appendages having been weighed, the apparatus is exhausted to a pressure of 1 cm. of mercury, or less. The flask is immersed in a water-bath at 50°, and the liquid serum is then allowed to enter slowly through the funnel as nearly as possible at the rate at which evaporation proceeds. So treated, the serum foams largely and leaves a friable product which adheres loosely to the walls of the flask. When the desired amount of liquid has been evaporated, the cold water of the condenser jacket is replaced by

warm water and air slowly admitted through the funnel. This is followed by re-exhaustion with slight raising of the temperature of the bath. When the serum is dry, the apparatus is dismantled and the parts weighed. Serum contains about 9% of solids, which, as thus obtained, dissolve readily in water, yielding a slightly turbid solution.

H. W. B.

**The Action of Ferric Thiocyanate on Normal Human Serum.** ARTHUR VERNES and ROGER DOURIS (*Compt. rend.*, 1918, 167, 972—974).—The reagent prepared by the action of ammonium thiocyanate or ferric chloride is added to a series of tubes containing 0.4 c.c. of diluted serum, in diminishing dilutions. The first tubes show no precipitation, then follow a series of tubes in which precipitation takes place, and these are followed by another series with no precipitation.

S. B. S.

**Mineral Metabolism in Experimental Acidosis.** KINCO GORO (*J. Biol. Chem.*, 1918, 36, 355—376).—The daily administration of hydrochloric acid to a rabbit during a period of from one to four weeks was accompanied by an increase in the urinary excretion of phosphoric acid. Subsequent investigation showed that the muscles were deficient in phosphorus, sodium, and potassium, and the bones in calcium carbonate. The fat content of the skeleton was also greatly reduced. These results indicate that in acid intoxication after the carbonates in the body fluids have been neutralised, the alkali phosphates of the muscles and the calcium carbonate of the bones are drawn on in the attempt to maintain the hydrogen-ion concentration of the body tissues at the normal level.

H. W. B.

**Comparative Metabolism of certain Aromatic Acids.**  
**II. Fate of *p*-Hydroxybenzoic Acid and *p*-Hydroxyphenylacetic Acid in the Organism of the Monkey.** CARL P. SHERWIN (*J. Biol. Chem.*, 1918, 36, 309—318. Compare A., 1917, i, 603).—Feeding experiments on a monkey (*Macacus rhesus*) indicate that in relation to the process of the metabolism of the aromatic amino-acids, the monkey stands in the same position as other lower animals and thus differs from man. The monkey excretes the *p*-hydroxybenzoic acid in the urine in an uncombined state, whilst a partial combination with glycine takes place in the human organism. On the other hand, *p*-hydroxyphenylacetic acid is partly excreted as *p*-hydroxyphenylacetic acid in the case of the monkey and lower animals, but is excreted in an uncombined form in man.

H. W. B.

**Metabolic Changes induced by the Administration of Guanidine Bases. V. Change of Phosphate and Calcium Content in Serum in Guanidine Tetany and the Relation between the Calcium Content and Dextrose in the Blood.** C. K. WATANABE (*J. Biol. Chem.*, 1918, 36, 531—546. Compare A., 1918, i, 327).—The administration of guanidine to rabbits produces a condition of severe acidosis with the retention of phosphates, a

decrease of calcium in the blood, and a hypoglycæmia. After the extirpation of the parathyroids in the rabbit, phenomena and symptoms are observed which are similar to those occurring after the administration of guanidine. Since there is a large increase in the guanidine bases in the blood in parathyroid and in idiopathic tetany, it is possible that the fundamental cause of tetany is the increased formation of guanidine brought about by the disturbance of the function of the parathyroids. H. W. B.

**Influence of Protein Feeding on the Concentration of Amino-acids and their Nitrogenous Metabolites in the Tissues.** H. H. MITCHELL (*J. Biol. Chem.*, 1918, **36**, 501—520).—The concentration of amino-acids, ammonia, and urea in the tissues of rats is comparable to that in the tissues of other mammals. In the young, growing animal the concentration of the amino-acids in the tissues is considerably higher than in the adult animal, due possibly to the greater metabolic activity of the young as compared to the adult tissues. The effect of feeding with protein depends also on the age of the animal; in young rats the concentration of the amino-acids and urea in the tissues is increased, whilst in the adult animal no or only a slight increase can be detected. H. W. B.

**Animal Calorimetry. XV. Further Experiments Relative to the Cause of the Specific Dynamic Action of Protein.** H. V. ATKINSON and GRAHAM LUSK [with G. F. SODERSTROM] (*J. Biol. Chem.*, 1918, **36**, 415—427. Compare Lusk, A., 1915, i, 614).—The administration of hydrochloric acid to a dog causes a slight increase in the basal metabolism, but a further increase is not observed when aspartic acid is simultaneously given. Aspartic acid, like glutamic acid, does not therefore exert any specific dynamic action. Asparagine and glycine behave very differently in metabolism, the former being without specific dynamic action, whilst the latter exerts the most powerful specific dynamic action of any of the amino-acids in protein which have been thus far tested. Therefore, the hypothesis of Grafe (*Deutsch. Arch. Klin. Med.*, 1915, **118**, 1) that the specific dynamic action of protein is due to the amino-radicles of the amino-acids is shown to be incorrect. Neither succinic acid nor acetamide is found to increase the heat production of the animal. The authors draw the conclusion that the processes of deamination and urea formation have nothing to do with the specific dynamic action of protein. H. W. B.

**Penetration of Neutral Salts into [Animal] Cells.** WILHELM VON MOELLENDORFF (*Kolloid Zeitsch.*, 1918, **23**, 158—163).—A number of experiments on the penetration of solutions of sodium chloride, manganese sulphate, uranium nitrate, and potassium sulphate into liver and kidney cells of animals are described. The experiments show that sufficient of the salts penetrate to produce an intracellular precipitation of the acid colour substances contained in the cells. This precipitation is identical with the action of neutral



salts on semi-colloids and is characterised as a diminution of the dispersion. The process indicates that the cell walls are permeable to neutral salts. The process is in keeping with the theory of a sponge-like structure for protoplasm. J. F. S.

**Synthetic Capacity of the Mammary Gland. I. Can this Gland Synthesise Lysine?** E. B. HART, V. E. NELSON, and W. PITZ (*J. Biol. Chem.*, 1918, **36**, 291—307).—Rats fed on a lysine-free diet of zein and tryptophan with non-nitrogenous substances are able to give birth to their young, but appear to be unable to rear them. It is considered that these results are due to the failure of the mammary glands of the rats to produce sufficient milk, owing to the absence of the lysine necessary for the formation of the protein normally present in rat's milk. H. W. B.

**Vitamine Studies. II. Does Water-soluble Vitamine Function as a Catalase Activator?** R. ADAMS DUTCHER and FERDINAND A. COLLATZ (*J. Biol. Chem.*, 1918, **36**, 547—550. Compare A., 1918, i, 561).—Vitamine extracts do not increase the catalytic activity of extracts of liver. The vitamine in the body does not act as a direct activator of catalase, but seems to stimulate the organism to greater production of the enzyme. H. W. B.

**Vitamine Studies. III. Curative Properties of Honey, Nectar, and Maize-pollen in Avian Polyneuritis.** R. ADAMS DUTCHER [with L. V. FRANCE] (*J. Biol. Chem.*, 1918, **36**, 551—553. Compare preceding abstract).—Honey contains a small amount of the water-soluble vitamine, but the amount is so small that its curative effect can only be observed after concentration of the vitamine by adsorption with siliceous earth. Nectar appears to be almost free from vitamins, but maize-pollen is relatively rich in this respect, small amounts of pollen extract being sufficient to cause the recovery of pigeons in the last stages of polyneuritis. It is possible that it is the presence of pollen grains in ordinary honey which confers on it its small curative power over polyneuritis. H. W. B.

**Quinine in Animal Tissues and Liquids, with Methods for its Estimation.** W. RAMSDEN, I. J. LIPKIN, and E. WHITLEY (*Ann. Trop. Med. Parasitol.*, 1918, **12**, 223—258. Compare Ramsden and Lipkin, A., 1918, ii, 251; Hartmann and Zila, A., 1918, i, 328).—The method previously described by Ramsden and Lipkin is applicable to the estimation of quinine in most tissues, but not in liver and brain. Given in large doses, the alkaloid accumulates in most tissues (particularly the suprarenals and kidneys) much more than in the blood, where three-fourths is in the serum but scarcely any in the red corpuscles; 90% of an intravenous dose leaves the blood in the first minute after injection. Quinine resists putrefaction in urine and faeces, but is rapidly attacked post mortem by the liver, presumably in a manner identical with the normal fermentative process of quinine metabolism during life. In a succession of large doses by the mouth more than 90% may be so metabolised. In

man there is considerable idiosyncrasy, both as regards the rate of excretion and the concentration in the blood; high concentration in the blood is associated with the symptoms of quinine intoxication. Quinotoxine is attacked by the liver like quinine, but some at least is excreted unchanged by the urine. G. B.

#### **Creatinuria. I. Exogenous Origin of Urinary Creatine.**

H. STEENBOCK and E. G. GROSS (*J. Biol. Chem.*, 1918, **36**, 265—289).—Experiments on pigs are described, the results of which indicate that creatine is formed from a precursor or precursors in the protein molecule. Urinary creatine has an exogenous origin only when the protein in the food happens to contain a large proportion of the creatine precursor. Feeding with excess of a protein containing a relatively small proportion of the creatine precursor may result in an inhibition of the production of creatine, on account of the accompanying diminution in protein katabolism effected by the agency of the non-nitrogenous portion of the protein of the food. In the discussion of the results attempts are made to reconcile the numerous apparently contradictory conclusions arrived at by other workers on this subject. H. W. B.

**Method for the Identification of certain Carbamido-acids in the Presence of Amino-acids and of Urea.** ALICE RONDE (*J. Biol. Chem.*, 1918, **36**, 467—474).—The method consists in decomposing the urea by urease, and then extracting the carbamido-acids, after acidifying with phosphoric acid, by means of ethyl acetate. The extract is then distilled with steam and the aqueous residue clarified with charcoal and then concentrated to small bulk. The crystals of carbamido-acid which separate are identified by the melting point, etc.

A method for the quantitative estimation of these acids by the Van Slyke process is based on the fact that the anhydrides formed from them are not decomposed by nitrous acid. The difference in the volumes of gas evolved before and after boiling the carbamido-acid solution with hydrochloric acid is a measure, therefore, of the amount of carbamido-acid present.

Applying these methods, it is found that after the injection of amino-acids into cats, carbamido-acids cannot be detected in the urine, whilst injected carbamido-acids are excreted in an unaltered form. Conjugation of amino-acids with urea preparatory to excretion does not seem, therefore, to occur in the animal organism.

H. W. B.

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### **Chemistry of Vegetable Physiology and Agriculture.**

**Autolysis of Starch.** W. BIEDERMANN (*Fermentforsch.*, 1918, **2**, 200; from *Chem. Zentr.*, 1918, ii, 738. Compare A., 1917, i, 62).—Boiled starch solutions after some weeks become infected with a bacterium which forms a sulphur-yellow pigment and hydrolyses

the starch to dextrose. The bacterium is possibly identical with, or at least closely related to, Schardinger's *Bacillus macerans*. The previously recorded autolysis of starch was probably due to infection with this micro-organism.

H. W. B.

**Azofication.** J. E. GREAVES (*Soil Sci.*, 1918, 6, 163—217).—A résumé of the literature on the subject of nitrogen fixation by *Azotobacter* and *Clostridium pasteurianum*. A full bibliography is appended.

W. G.

**Influence of certain Conditions on the Comparative Consumption of Dextrose and Lævulose by *Sterigmatocystis nigra*, starting from Sucrose.** MARIN MOLLIARD (*Compt. rend.*, 1918, 167, 1043—1046).—Using a culture liquid in which the nitrogen is entirely supplied by one ammonium salt and the ratio nitrogen:carbon is 1:16, it is found that the ratio of dextrose to lævulose consumed is considerably increased by the presence of acid. Similarly, the ratio dextrose to lævulose consumed is increased if the ratio nitrogen:carbon is diminished to 1:160. In each of these cases, the weight of mycelium obtained in a given time is also diminished. It is considered that lævulose plays the principal part in the building up of the tissues.

W. G.

**Capacity of Alcohols and Acids to Sustain the Growth of Yeasts and other Common Fungi.** TH. BOKORNY (*Allg. Brau Hopf. Zeit.*, 1917, 747; from *Bied. Zentr.*, 1918, 47, 191).—The author has collected information regarding the behaviour of fungi, yeasts, and bacteria when cultivated in media containing various alcohols and acids. All acids exert an inhibiting action on fermentation when the concentration is increased to a certain limit, which differs for each substance. Formic and oxalic acids are specially toxic. Bases are more poisonous than acids towards yeast.

H. W. B.

**Quantitative Estimations of the Enzymic Activity of Living Cells.** I. H. EULER, O. SVANBERG, and S. HEINTZE (*Fermentforsch.*, 1918, 2, 194—199; from *Chem. Zentr.*, 1918, ii, 746).—At 16°, an increase in  $p_H$  from the optimum for yeast invertase (5·07 to 4·67) to 7·7 reduces the activity of the invertase from 0·067 to 0·007.

H. W. B.

**Influence of certain Substances Extracted from Yeast by Alcohol on the Activity of the Yeast Enzymes.** EMIL ABERHALDEN and H. SCHAUMANN (*Fermentforsch.*, 1918, 2, 120—151; from *Chem. Zentr.*, 1918, ii, 737—738).—An extract of yeast, prepared by boiling with 10% sulphuric acid and subsequently treating with alcohol, exerts an accelerating action on the enzymic cleavage of sucrose and maltose and on the fermentation of dextrose, lævulose, and particularly galactose by yeast. The fermentation of lactose is not affected. The activity of carbonylase is increased. The accelerative action of the extract is observed, not only with living yeast, but in the cases of dried yeast and pressed yeast juice. Various fractions can be prepared from

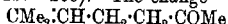
the extract possessing diverse degrees of activating power, one of the more powerful being termed "autonin." This latter substance is prepared by precipitation of the alcoholic extract with acetone, and is completely free from phosphorus. The author suggests that vitamins may resemble these extracted substances in exerting an activating influence on certain enzymic processes in the body.

H. W. B.

**Behaviour of Yeast towards various Carbohydrates in various Concentrations, and the Effect of the Addition of Amino-acids on the Fermentation.** EMIL ABERRHOLDEN (*Fermentforsch.*, 1916, 229; from *Bied. Zentr.*, 1918, 47, 190).—The extent of alcoholic fermentation is not affected when the concentration of the sucrose in the solution is increased from 10 grams to 30 grams per 250 c.c. The loss in weight is greater when alanine is added to the sucrose solution. When dextrose is substituted for sucrose, the extent of fermentation is found to vary with the concentration of the carbohydrate. When dried yeast is employed, a distinct latent period precedes the onset of fermentation.

H. W. B.

**Phytochemical Reductions. XIV. Hydrogenation of a Ketone by Yeast. Change of Methylheptenone into the Corresponding Heptenol.** C. NEUBERG and A. LEWITE (*Biochem. Zeitsch.*, 1918, 91, 257—266).—The change



into  $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$  takes place to the extent of about 10%. The product is sometimes levorotatory and at other times dextrorotatory. There is produced at the same time an equimolecular proportion of acetaldehyde. The ketone appears to compete with this product, formed as an ordinary intermediary product of alcoholic fermentation, for the available hydrogen.

S. B. S.

**Excitation of Ferment Action.** WOLFGANG WEICHARDT and HERMANN APITZSCH (*Biochem. Zeitsch.*, 1918, 90, 337—347).—A criticism of certain statements in literature with regard to excitation of ferment action, with some demonstrations of sources of error in methods of manipulation in experiments on which certain statements are founded. These refer more especially to the measurement of catalase action volumetrically, to the difficulties of measuring the same amounts of catalase (or blood), and to the errors in the estimation of the action of urease due to the neglect of hydrolysis of carbamide while distilling off the ammonia.

S. B. S.

**The Influence of Aluminium on the Germination of Seeds and the Development of Plants.** JULIUS STOKLASA with J. ŠEBOR, W. ZDOBNICKÝ, F. TÝMICH, O. HORÁK, A. NĚMEC, and J. ČWACH (*Biochem. Zeitsch.*, 1918, 91, 137—223).—This communication contains a very detailed account of the action of aluminium, manganese, and iron on the germination of seeds and the development of the plants. It indicates, generally, that very

small amounts of aluminium salts exert a favourable influence on the germination of seeds, whereas larger amounts exert a toxic action. Similar remarks apply to salts of manganese. When large amounts of manganese salts exert a toxic action, an antagonistic effect can be produced by aluminium salts when the concentration of the latter is not too high, and the toxic effect of both ions comes into play. A study of the action of these various salts when used in the nutrient solutions for growing plants indicated that aluminium is very toxic to xerophytes, whereas the hydrolytes and hygrophytes show a considerable resistance. As regards the mesophytes, a toxic action could be determined in the case of iron ions which could be antagonised by aluminium. Aluminium and manganese ions in sufficiently low concentrations, both together or alone, produce a favourable effect on growth; higher concentrations act toxically. There is no antagonistic action as regards toxicity of iron and manganese. The authors deduce from their results a mathematical expression for the growth curves, and develop a general theory of the action of chemical reagents on growth. Measurements were made of the electrical conductivities of the salts employed, and comparisons instituted between the intensity of action of the various ions and the dissociation grade of the salts; a considerable parallelism was found to exist between this physiological intensity of action and the conductivities of the salt solutions.

S. B. S.

**Catalase and Oxydase Content of Seeds in Relation to their Dormancy, Age, Vitality, and Respiration.** WILLIAM CROCKER and GEORGE T. HARRINGTON (*J. Agric. Res.*, 1918, 15, 137—174).—The concentration of solutions of hydrogen peroxide may readily be measured by determining the volume of oxygen liberated on the addition of an excess of powdered seeds containing plant catalase. Similarly, the catalase activity of seeds may be measured by using an excess of hydrogen peroxide, but in this case the latter solution must first be made neutral to phenolphthalein by the addition of  $N/10$ -sodium hydroxide. The authors have carried out a general investigation as to the conditions affecting catalase and oxydase activity of seeds, and find that in certain seeds there is a close correlation between catalase activity and respiratory intensity, but no correlation between these two factors and the vitality of the seeds or the vigour of the resulting seedlings. They find that general conclusions cannot be drawn as to the catalase behaviour in all seeds, but it seems probable that seeds can be separated into several physiological types, for each of which more or less general conclusions can be drawn. Catalase activity of seeds seems to agree more closely and generally with physiological behaviour than does oxydase activity. [See, further, *J. Soc. Chem. Ind.*, 1919, February.] W. G.

**Distribution of the Mineral Elements and Nitrogen in the Etiolated Plant.** G. ANDRÉ (*Compt. rend.*, 1918, 167, 1004—1006).—The author has investigated the proportions of

mineral matter and nitrogen which pass, during etiolation, from the cotyledons into the plantule in seeds germinated in the dark in an inert medium. The seeds used were white haricot, germinated in sand previously extracted with acid and calcined. After twenty-five days, the stems being 30—35 cm. in length, the plants were removed and their roots washed. Their cotyledons were separated from the stem and roots and weighed separately, and then analysed. The major portion of the calcium remained in the cotyledons, whilst the magnesium, and to a still greater extent the potassium, had migrated to the roots and stem. Nearly 75% of the phosphoric acid and nitrogen were transported from the cotyledons to the plantule, and the migration of the sulphur was very similar.

W. G.

**Mechanism of Assimilation Processes.** K. SCHAUM (*Ber.*, 1918, 51, 1372—1375).—The conclusions recorded by Willstätter and Stoll (*A.*, 1918, i, 207) had been drawn previously by the author (*Sitzungsber. Ges. Beförd. gesamt. Naturwiss. Marburg*, 1907, 158).

C. S.

**Colloidal Properties of Protoplasm. Imbibition in Relation to Growth.** FRANCIS E. LLOYD (*Trans. Roy. Soc. Canada*, 1917—18, [iii], 11, 133—139).—Living protoplasm, as such, behaves towards acids and alkalis in a manner sufficiently like that of gelatin to warrant the view that imbibition is a factor in growth. The results in growth are called forth by much lower concentrations of the reagents; this is probably due to the different nature of the emulsoids involved.

J. F. S.

**Conductivity as a Measure of Permeability.** W. J. V. OSTERHOUT (*J. Biol. Chem.*, 1918, 36, 485—487).—Experiments are described which are designed to elucidate whether when an electric current passes through a tissue, any of the current passes through the protoplasm or all through the intercellular substance. Employing a green marine alga (*Ulva*) and a marine flowering plant (*Zostera*), both with cellulose walls, it is found that after killing by methods which do not produce irreversible changes in the properties of cellulose, the conductivity rises to a constant value and is not thereafter affected by exposure to reagents which produce great alterations in the conductivity of living tissues. Moreover, the temperature-coefficient of the electrical conductivity of living tissue differs from that of dead tissue, and the effect of placing a tissue in contact with a strong calcium chloride solution is not an increase in the conductivity, but a decrease on account of the diminished conductivity of the protoplasm killed by the salt more than counterbalancing the increased conductivity of the intercellular tissues. The alterations of conductivity observed in living tissue are due, therefore, to changes in the protoplasm, and not to changes in the non-living intercellular substance, and as the results obtained by the electrical method are in complete agreement with those obtained by other methods for measuring permeability, such as exosmosis.

diffusion through membranes of living tissue, etc., the author draws the conclusion that the electrical conductivity is a measure of the permeability of the protoplasm of the cell. H. W. B.

**of Diffusion on the Conductivity of Living Tissue.** OSTERHOUT (*J. Biol. Chem.*, 1918, **36**, 489—490).—Electrolytes with univalent cations usually produce an increase in the conductivity of living tissues, whilst those with bi- or trivalent cations first diminish and then increase the conductivity. Apparent exceptions to this rule have been noted, and these have been shown to be due to the effect of diffusion. Thus, on transfer of tissue of *Laminaria* from sodium chloride to rubidium chloride solution of the same conductivity, the molecules of sodium chloride diffuse out of the tissue more rapidly than the larger molecules of rubidium chloride can diffuse inward. Hence there is a temporary deficiency of salt in the tissue, and the conductivity immediately falls. Reverse effects are produced on transference into sodium chloride solutions. H. W. B.

**Method of Measuring the Electrical Conductivity of Living Tissues.** W. J. V. OSTERHOUT (*J. Biol. Chem.*, 1918, **36**, 561—568).—Various types of apparatus are figured and described which permit of the measurement of the electrical conductivity of pieces of living tissue or of intact organisms. Successive measurements do not vary more than 1% from the mean value. H. W. B.

**The Absorption Curve of the Green Colouring Matter in Living Leaves.** A. URSPRUNG (*Ber. Deut. bot. Ges.*, 1918, **36**, 73—85).—The absorption curve has been determined by the thermoelectric method for the green pigments in a living leaf of *Tradescantia*. A very slight absorption occurs in the green part of the spectrum, which increases towards the red and the violet ends, reaching a maximum in the violet, which is greater than that occurring in the red. Towards the red end of the spectrum the absorption curve reaches a maximum point between *B* and *C*, and then falls rapidly towards the ultra-red. H. W. B.

**Significance of the Wave-length for Starch-formation (in the Green Leaf).** A. URSPRUNG (*Ber. Deut. bot. Ges.*, 1918, **36**, 86—100. Compare preceding abstract).—A comparison of the absorption curve with one indicating the extent of formation of starch in the green leaf reveals a close parallelism extending from the ultra-red to the green part of the spectrum. From this point towards the violet, marked divergence is observed; the absorption increases to a maximum, whilst the starch-formation greatly diminishes. It is probable that the latter phenomenon is occasioned by the action of the ultra-violet light on the stomata, which results in the reduction of the supply of carbon dioxide for photo-synthetic purposes. In a few experiments with leaves containing no stomata,

the parallelism between absorption and starch-formation could be established as far as the bluish-violet part of the spectrum.

H. W. B.

**Microchemistry of Plants. X. Siliceous Bodies in the Epidermis of *Campelia Zanonía*, Rich. XI. Crystalline Carotin in the Cup of *Narcissus poeticus*.** HANS MOLISCH (*Ber. deut. bot. Ges.*, 1918, **36**, 277—281, 281—282).—Siliceous bodies, similar to those discovered by Möbius (*Wiesner-Festschrift*, Vienna, 1908, p. 81) in the leaves of *Callisia repens*, are present in the epidermis of *Campelia Zanonía*. They occur in small cells in the leaves and stalks, and are insoluble in acids, except hydrofluoric acid. When the leaf is immersed in phenol solution or in Millon's reagent, the bodies assume a peculiar red hue, which renders them very apparent. These two *Commelina*, therefore, are related, not only botanically, but also in a pronounced chemical manner.

The red colour in the rim of the cup of *Narcissus poeticus* is found to be due to the presence of accumulations of carotin crystals in the cells.

H. W. B.

**The Phenol of the Leaves of *Coleus amboinicus*, Lour (*C. Carnosus*, Hassk.).** F. WEEHUIZEN (*Rec. trav. chim.*, 1918, **37**, 355—356; *Pharm. Weekblad*, 1918, **55**, 1470—1472).—The essential oil of *Coleus amboinicus* contains a phenol which the author has identified as carvacrol.

W. G.

**Presence of Hydrogen Cyanide in a Fern, *Cystopteris alpina*.** MARCEL MIRANDE (*Compt. rend.*, 1918, **167**, 695—696).—The fern, *Cystopteris alpina*, Desv., contains in its leaves a cyanogenic glucoside which under the influence of an enzyme, also contained in the plant, is hydrolysed, and yields hydrogen cyanide and benzaldehyde. The proportion of hydrogen cyanide given by the leaves is lowest in the early part of September (for example, 0.011%).

C. A. M.

**Production of Glycine by *Isaria densa*.** MARIN MOLLIARD (*Compt. rend.*, 1918, **167**, 786—788).—The fungus *Isaria densa*, when cultivated on gelatin decomposes it, giving glycine, the yield of this amino-acid being equivalent to 33% of the gelatin decomposed, whereas by acid hydrolysis gelatin only yields 16.5% of glycine. Similarly, this fungus decomposes fibrin, giving 38% of glycine, and also ovalbumin, serum-albumin, and casein, giving on an average 33.6% of glycine.

W. G.

**Sterilised Poppy Juice.** L. REUTTER DE ROSEMONT (*Schweiz. Apoth. Zeit.*, 1918, **56**, 55—56; from *Chem. Zentr.*, 1918, ii, **89**, 736—737).—The results indicate that certain alkaloids exist pre-formed in poppy juice and are not the products of subsequent fermentation processes. On distillation in a vacuum, poppy juice



gives off formic and acetic acids, and, after subsequent treatment with sodium hydroxide, ammonia, pyrrolidine, and methylpyrrolidine. By extraction of the tarry residue, several basic substances, including codeine but not morphine, are obtained. Light petroleum extracts pyrrolidine, benzene, a yellow liquid,  $(C_8H_9O_4N)_2$ , aurichloride, m. p.  $231^\circ$ , chloroform, a yellowish-brown powder,  $(C_8H_7O_9N)_x$ , and amyl alcohol, a solid alkaloid  $(C_2H_3O_5N)_2$ . The residue is soluble in dilute hydrochloric acid, and from the solution sodium hydroxide precipitates a colourless substance,  $(CHO_3N)_2$ . Lactic, meconic, and oxalic acids, together with dextrose, were also detected in the original juice. H. W. B.

**Vegetable and Animal Fats and Waxes. II.** ALBERT B. WEINHAGEN (*Zeitsch. physiol. Chem.*, 1918, 103, 84—86. Compare A., 1918, i, 56).—The solid fat isolated from rice bran does not contain any glycerol, whilst the liquid oil contains only about 1.7%. H. W. B.

**Oxydases: with Special Reference to their Presence and Function in the Sugar-cane.** RAMJI NARAIN (*Agric. J. India*, 1918, 47—64).—Laccases and aldehydase are found to be present in the cane, but tyrosinase is absent. The author finds that the direct guaiacum reaction depends more on the presence of a peroxide than on that of catechol. As a preservative for oxydases, chloroform is far more satisfactory than either ether or toluene. In the cane the lower portions show a greater oxydase activity than the upper portions, and thus the oxydases are stronger in that part of the plant where the sugar is stored. Similarly, the leaf and the adjoining green portion of the cane are richer in oxydase than the stem. The oxydases are not destroyed by boiling the extract containing them for fifteen minutes, although they take some time to recover their activity after cooling. Similarly, a reducing agent such as hydrogen sulphide only temporarily inhibits their activity but does not destroy it permanently. The author considers that oxydases are not enzymes in the true sense of the word. W. G.

**Gaseous Products of the Putrid Fermentation and the Odour of Truffles.** I. GUARESCHI (*Gazzetta*, 1918, 48, ii, 98—106).—The gaseous or highly volatile products emitted during the putrefaction of truffles are mostly absorbable by soda lime (compare A., 1916, ii, 324, ¶2). Those not so absorbed have the odour of the fresh truffle, such odour being due to one or more gases or volatile compounds, which are formed by the putrefactive alteration of the proteins, but are not yet identified. T. H. P.

**Action of Coal Gas on Plants. IV. Action of Coal Gas on the Root Systems of Trees. Cause of the Action of the Gas.** C. WEHMER (*Ber. Deut. bot. Ges.*, 1918, 36, 140—150. Compare A., 1917, i, 618).—The experiments on the effects produced by passing gas through soil containing the roots of plants have been

extended to small trees in pots. It is found that the effect produced is dependent on the season of the year in which the experiment is performed; it completely kills the tree in the spring; in autumn the leaves fall off, but the tree remains alive, whilst in winter no pernicious effect is observable. When the soil is replaced by a solution of salts, similar toxic effects are observed. The toxicity appears to be due to one or more constituents of the gas, and not to mere absence of oxygen. Any treatment of the gas which removes its peculiar odour also abolishes its toxicity, a result which seems to show that the toxic agent is that constituent of the gas which confers on it its characteristic odour.

H. W. B.

**Soil Acidity as Affected by Moisture Conditions of the Soil.** S. D. CONNER (*J. Agric. Res.*, 1918, 15, 321—329).—The acidity of acid soils, kept under different conditions of moisture in pots for a year, varied with the different conditions of moisture for a given soil. Soils rich in organic matter showed the greatest acidity after being kept fully saturated, whilst soils poor in organic matter showed the greatest acidity after being kept half-saturated. The potassium nitrate extract from the fully saturated soils contained more soluble ferrous iron and manganese, but less aluminium, than the other soils. Thus the measurable acidity of acid soils varies to a large degree under different conditions of moisture and aeration, but this variation is due to chemical rather than to physical changes in the soil.

W. G.

**Determining the Absolute Salt Content of Soils by Means of the Freezing-point Method.** GEORGE J. BOUYOUCOS and M. M. MCCOOL (*J. Agric. Res.*, 1918, 15, 331—336).—The authors find that at a comparatively high content of moisture, the influence of the unfree water on the concentration of the soil solution is practically negligible. The freezing-point method can therefore be used to determine the absolute salt content of soils by bringing them to a suitable content of moisture before determining the depression of the freezing point. [For details, see *J. Soc. Chem. Ind.*, 1919, February.]

W. G.

**Hydrogen-ion Concentration—Soil Type—Common Potato Scab.** LOUIS J. GILLESPIE and LEWIS A. HURST (*Soil Sci.*, 1918, 6, 219—235).—The authors find that the electrometric method (compare Gillespie, A., 1916, i, 303) and the colorimetric method of Clark and Lubs (compare *J. Bact.*, 1917, 2, 1, 109, 191) for determining hydrogen-ion concentration of soils give results which are in agreement within the limits of experimental error. It is necessary to add 1 or 2 c.c. of water to each gram of air-dry soil, but this addition of water does not seem to be a serious limitation. From an examination of a large number of soils the authors find a close correlation between the hydrogen-ion exponent and the occurrence of common potato scab. With an exponent below 5.2, scab seldom appears, but with exponents much above this figure the potatoes are generally scabbed.

W. G.

**Chlorine Index as a Comparative Measure of the Richness of Soils in Humus.** L. LAPICQUE and E. BARRÉ (*Compt. rend.*, 1919, 168, 118—121).—The authors find that the amount of an aqueous solution of sodium hypochlorite decomposed in a given time by a given volume of soil varies considerably with the soil taken, and that this estimation forms a rough method of placing the soils in the order of their probable richness in humus, the volume of chlorine liberated varying directly with the humus content of the soil.

W. G.

**Importance of Mould Action in the Soil.** SELMAN A. WAKSMAN (*Soil Sci.*, 1918, 6, 137—155).—Moulds have been isolated in large numbers from cultivated and uncultivated soil. By the growth of their mycelia, changes in the organic and inorganic constituents of the soil are brought about, but no nitrification or fixation of nitrogen is effected. Not much ammonia is produced in the presence of available carbohydrate as a source of energy, as it is absorbed in the formation of mould protein, but in the absence of carbohydrate considerable amounts of ammonia are left in the soil. Carbohydrates are decomposed with the formation of carbon dioxide. Moulds exercise an unfavourable effect on soil fertility in that they compete with green plants for available nitrogen compounds. On the other hand, they exercise also a beneficial effect on account of their large production of enzymes and acids, which produce further changes in soil constituents favourable to the growth of green plants. [See *J. Soc. Chem. Ind.*, 1919, February.]

J. H. J.

**Nitrogen Compounds in Rain and Snow.** FRANK T. SHUTT and R. L. DORRANCE (*Trans. Roy. Soc. Canada*, 1917—1918, [iii], 11, 63—72).—A series of analyses of snow and rain which have fallen in or near Ottawa during the years 1908—1917 is recorded. The analyses deal with the nitrogen compounds, and are expressed as parts of nitrogen per million as (i) free ammonia, (ii) albuminoid ammonia, (iii) nitrates and nitrites. The average of these for the ten years is 0.461 nitrogen as free ammonia, 0.138 as albuminoid ammonia, 0.277 as nitrite and nitrate. This corresponds with 6.583 lb. of nitrogen per acre. A further analysis of the results for the various months is also given, from which it is shown that snow is decidedly poorer in all forms of nitrogen compounds than rain (compare A., 1915, i, 636).

J. F. S.

**Composition of the Waters of the Inter-Mountain Region.** J. E. GREAVES and C. T. HIRST (*J. Ind. Eng. Chem.*, 1918, 10, 1001—1004).—Analyses of a large number of river waters are recorded, the majority of which are used for irrigation purposes. Whilst some of the waters are free from objectionable constituents, others, although good at their source, were found to contain large quantities of alkali sulphates, etc., after flowing through a district rich in soluble salts. The effect of these saline waters on vegetation is discussed.

W. P. S.

## General and Physical Chemistry.

**The Optical Behaviour of Water of Crystallisation.**

KÄTHE BRIEGER (*Ann. Physik*, 1918, [iv], 57, 287—320).—Experiments have been made to compare the reflection intensities of crystals of a number of hydrated salts in the infra-red region,  $\lambda = 2.5$ — $7.0 \mu$ , with that of water. The reflection curve for water shows a well-marked maximum intensity at  $\lambda = 3.07 \mu$ , and very similar maxima are found for hydrated crystals (compare Schaefer and Schubert, A., 1916, ii, 505). Of the nine isomorphous alums examined, eight show two maxima in the intensity curves in place of the single water maximum at  $3.07 \mu$ , their positions being near  $3.02 \mu$  and  $3.51 \mu$ , but differing slightly in the different alums. The curve for caesium alum, however, shows a third maximum, and in this respect is abnormal. The water maximum at  $\lambda = 6.22 \mu$  also becomes doubled in the case of the alums.

As examples of uniaxial crystals, the hexahydrated nickel sulphate and selenate (tetragonal trapezohedral) were examined. In the case of these salts, the water maximum is shifted only slightly. The intensity of the reflection depends on the position of the optic axis relative to the reflecting surface, the water of crystallisation exhibiting dichroism. Similarly in the case of monoclinic crystals of the magnesium sulphate and zinc-ammonium sulphate groups, the reflection properties are closely related to the optical properties, the water being trichroic. It is concluded that the symmetry properties of the water in hydrated salts correspond with the symmetry of the crystals. The bearing of the results on Werner's theory of the constitution of hydrated salts is discussed.

Preliminary experiments with analcime indicate a shift of the water maximum towards the shorter wave-lengths, whilst in every other case the shift is in the other direction. Further experiments may be expected to throw light on the constitution of the zeolites generally, especially with regard to the state of combination of the water which they contain.

E. H. R.

**Effect of the Electric Field on Spectrum Lines. VII.**

**The Fowler Helium Series.** J. STARK, O. HARDTKE, and G. LIEBERT (*Ann. Physik*, 1918, [iv], 56, 569—576. Compare Fowler, A., 1913, ii, 811).—The effect of an electric field on the lines  $\lambda 3203$  and  $\lambda 2733$  of the Fowler helium series has been studied. The effect is compared with that on the Balmer hydrogen series, and it is shown that both effects are very similar, the lines in both cases being symmetrically resolved into their components. The intensity of the two components is equal.

J. F. S.

**Effect of an Electric Field on Spectrum Lines. VIII. New Principal Series of Helium Lines which Appear in the Electric Field.** J. STARK (*Ann. Physik*, 1918, [iv], 56, 577—588. See preceding abstract).—During an investigation of

the influence of an electric field on the helium spectrum, two new

principal series of lines were discovered. The lines of the first of these, the He I principal diffused series, are given by the formula  $\nu = Ez(h) - Lz(m, d)$ . In the electric field, the lines of this series are resolved in such a way that the components do not lie symmetrically, but are displaced about 1 Å. unit in the direction of shorter wave-lengths. The second new series of helium lines, the He I sharp series, is represented by the formula  $\nu = Ez(h) - Lz(m, s)$ . The lines of this series in an electric field were not resolved into several components, but were displaced towards the longer wave-lengths. The He<sup>+</sup> ion possesses twelve series, which can be arranged in two systems of six series. In each system there are three principal series with the same end-number, and three subsidiary series, also with the same end-number. J. F. S.

**Effect of an Electric Field on the Ultra-violet Lines of Helium.** G. LIEBERT (*Ann. Physik*, 1918, [iv], 56, 589—609. See preceding abstracts).—The ultra-violet lines of the principal series He I are displaced towards the red end of the spectrum under the influence of an electric field. Both the components undergo the same amount of displacement. The lines of the second subsidiary series are displaced without resolution toward the red by an electric field. In this case, the displacement is rather more than the proportional amount. The lines of the principal series He II are displaced toward shorter wave-lengths by an electric field. In the case of the third subsidiary series of He I, a displacement of the lines toward longer wave-lengths is brought about by an electric field. J. F. S.

**A New Helium Series under the Influence of an Electric Field.** G. LIEBERT (*Ann. Physik*, 1918, [iv], 56, 610—616).—Corresponding with the third He I series, a subsidiary He II series becomes visible in a strong electric field, whereas in a weak electric field it has no noticeable intensity. The electric effect on every member of the principal series corresponds with the effect on the similar member of the subsidiary series. The lines of the subsidiary series, like those of the principal series, are displaced toward the shorter wave-lengths. J. F. S.

**Spectrum of the Chromosphere. An Eruptive Protuberance of the 6th July, 1917.** P. CARRASCO (*Anal. Fis. Quim.*, 1918, 16, 700—706).—A comparison of the author's observations of the chromosphere spectrum with the results of Rowland and of Adams. The presence of the helium series 6678·1, 4922·1, etc., is noted as a characteristic of the spectrum. The helium series 7665·6, 4713·2, etc., was not observed. W. S. M.

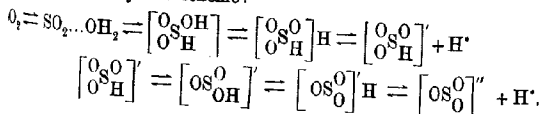
**Optical Researches on the Constitution of Sulphurous Acid, its Salts and Esters.** KONR. SCHAEFFER [with WILLY KÖHLER] (*Zeitsch. anorg. Chem.*, 1918, 104, 212—250).—Aqueous solutions of sulphur dioxide show an absorption band in the ultra-violet in the same position as the band given by sulphur dioxide gas, although somewhat broader. Beer's law is not followed, the

band becoming much shallower with increasing dilution. The absorbing substance in aqueous solutions is a hydrate of sulphur dioxide,  $\text{SO}_2 \dots \text{OH}_2$ , which appears to be more active than sulphur dioxide itself. Since the normal sulphites and the sulphite esters,  $\text{Et} \cdot \text{SO}_2 \cdot \text{OEt}$  and  $\text{SO}(\text{OEt})_2$ , are both transparent in the ultra-violet, it is concluded that sulphurous acid itself is non-absorbing, both in the unionised and ionised condition. The diminished absorbing power of solutions of sulphur dioxide on dilution is attributed to a change of equilibrium from left to right in the equation  $\text{SO}_2 \dots \text{OH}_2 \rightleftharpoons \text{H}_2\text{SO}_3$ . The aqueous solution contains very little sulphurous acid, and it is considered that measurements of the ion concentration in sulphur dioxide solutions have given rise to false ideas regarding the degree of dissociation of sulphurous acid, and consequently of the strength of the acid.

At higher temperatures, solutions of sulphur dioxide absorb more strongly, owing to a shift in the equilibrium of the above equation towards the left. Similarly, addition of sulphuric acid to an aqueous solution of the gas increases the depth of the band in the same manner, but only to a certain limit. When the sulphuric acid exceeds 5*N*, the absorption again decreases, probably owing to dehydration, in the sense  $\text{SO}_2 \dots \text{OH}_2 \rightarrow \text{SO}_2 + \text{H}_2\text{O}$ , the free sulphur dioxide being a less strong absorber than its hydrate. In pentane and chloroform solutions, the absorption is similar to that of the free gas, and the solutions follow Beer's law. In solutions of methyl and ethyl alcohols and ethyl ether, the absorption is much increased, and in the case of ethyl ether the band passes into general absorption in the ultra-violet. These solutions also follow Beer's law, and it is concluded that stable compounds of the type  $\text{O}_2\text{S} \dots \text{OHEt}$  and  $\text{O}_2\text{S} \dots \text{OEt}_2$  must be present in such solutions.

Normal sulphites show only end absorption in the extreme ultra-violet, and when a solution of a normal sulphite solution is half neutralised with sulphuric acid, the resulting metal hydrogen sulphite solution at first shows only end absorption, but after a few days, particularly under the influence of light, the sulphur dioxide band develops. When the metal hydrogen sulphite is formed, however, by mixing solutions of sulphur dioxide and normal sulphite, the band is present immediately. A solution of potassium pyrosulphite when freshly prepared shows only end absorption in the extreme ultra-violet, but the band gradually develops. Similarly, sodium methyl sulphite, which in methyl alcohol shows only end absorption, in aqueous solution gradually develops the sulphur dioxide band, more quickly in stronger solutions, owing to hydrolysis into sodium hydrogen sulphite and methyl alcohol.

The equilibrium conditions in aqueous sulphur dioxide solutions are represented by the scheme:



The hydrogen sulphite ion,  $\text{HSO}_3^-$ , is probably unstable and undergoes transformation into sulphurous acid and  $\text{SO}_3^{--}$ , thus:  $2\text{HSO}_3^- = \text{SO}_3^{--} + \text{H}_2\text{SO}_3$ . The sulphurous acid then comes into equilibrium with sulphur dioxide hydrate in the sense  $\text{H}_2\text{SO}_3 \rightleftharpoons \text{SO}_2 \cdots \text{H}_2\text{O}$ . These changes would explain the gradual development of the absorption band in hydrogen sulphite solutions. The view is expressed that the sulphite ion,  $[\text{SO}_3]^{--}$ , has a symmetrical constitution, and hence also the normal sulphites. This view is supported by the observation that selenious acid and the dialkyl selenites have similar absorption spectra to the normal sulphites (compare A., 1917, ii, 61, 186; 1915, ii, 389). E. H. R.

**The Ethylene Chromophore.** H. LEY (*Ber.*, 1918, 51, 1808—1819. Compare Ley, A., 1917, i, 261; Kauffmann, *ibenda*, 391).—The absorption spectra of styrene, stilbene, and cinnamic acid and their derivatives have been studied. Bathochromic effects are produced by the introduction of a methyl, methoxy- or ethoxy-group in the  $\omega$ -position in styrene, whilst a hypsochromic effect results when the methyl or ethoxy-group is substituted in the  $\alpha$ -position; hypsochromic effects are also observed with 7-methylstilbene,  $\beta$ -methylcinnamic acid,  $\beta$ -ethoxycinnamic acid, and  $\alpha$ -methylcinnamic acid as compared with the parent substances.

Attempts are also made to connect absorptiometric anomalies with abnormal values for the molecular refraction. The esters of  $\alpha$ - and  $\beta$ -methylcinnamic acid are less absorbent than the parent substance and have lower values for the exaltation  $\Sigma\alpha$ .  $\beta$ -Methylstyrene has an absorption similar to that of styrene, and its refraction anomaly is of the same order. With the hydroxy-derivatives a somewhat similar parallelism is observed, the hypsochromic effect of the ethoxy-group in the  $\alpha$ -position corresponding with a distinct diminution of the exaltation. Since, in general, an increase in refractive and dispersive power corresponds with an increase in the unsaturated nature of the compound, the explanation of the "disturbing" action of substituents on the absorption spectra of substances by the assumption of alteration in the degree of unsaturation appears to receive further support.

The extinction-coefficients of chloroform solutions of 1:3:5-trinitrobenzene and styrene,  $\alpha$ -ethoxystyrene,  $\beta$ -ethoxystyrene, and  $\beta$ -methoxystyrene respectively have also been measured, but the results scarcely lead to a definite conclusion.

Kauffmann's criticism of the author's views (*loc. cit.*) is reviewed. H. W.

**Crystalloluminescence. II. Triboluminescence and Crystalloluminescence.** HARRY B. WEISER (*J. Physical Chem.*, 1918, 22, 576—595. Compare A., 1918, ii, 419).—For the further investigation of the relationship between crystalloluminescence and triboluminescence, the phenomena have been studied with crystals of arsenic trioxide and the double sodium-potassium sulphate,  $2\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$ . In each case the colour of the light emitted by the crystals during rapid formation (crystalloluminescence) and that

produced by rubbing or crushing the crystals (triboluminescence) have been determined by photographing through an appropriate series of light filters, and it is shown that the light rays resulting from the two phenomena are identical in colour, that from arsenic trioxide differing considerably, however, from that from the double salt. The colour of the luminescence is therefore a specific property of the compound. The phenomena are held to be chemical in origin. Crystalloluminescence, which is only exhibited by a few inorganic compounds, is due to the rapid re-formation of molecules broken up by the process of electrolytic dissociation. Triboluminescence is due to the re-formation of molecules broken up by the violent disruption of crystals. Whilst all crystalloluminescent substances are also triboluminescent, the reverse is not true. In certain newly-formed crystals a state of strain may exist, and if outside force is applied to such crystals before the internal forces have become adjusted, violent disruption of the crystal may ensue, with consequent molecular decomposition and triboluminescence. The intensity of the triboluminescence depends on the force needed to break up the molecule and the magnitude of the conversion factor for light in the luminescent reaction.

E. H. R.

#### **Spectrum of the Ruby and Emerald. IV. Spectrum Phenomena in the Chromium Compounds.**

JAMES MOIR (*Trans. Roy. Soc. S. Africa*, 1918, 7, 129—130).—It has been shown previously (*ibid.*, 2, 321; 3, 271, 273; 4, 339) that the almost unique spectra of ruby and emerald are due to chromium oxide which has been compelled to vibrate in an abnormal or constrained manner leading to the production of narrow absorption bands; the constraining substance in the case of the ruby is crystalline alumina and in the case of the emerald it is glaucinum silicate. The present communication describes attempts to induce the constrained vibration of ordinary chromium oxide by artificial means. Suitable methods consist in dissolving chromic oxide in concentrated sulphuric acid and gradually adding an organic substance, such as starch, until the orange colour has changed to deep green or, more strikingly, by replacing the sulphuric acid by glacial phosphoric acid. It would appear possible to get a very close imitation of the emerald spectrum by the latter process, but the ruby spectrum, on the other hand, has not been reproduced except by means of alumina.

Concentrated hydrochloric, nitric, perchloric, formic, acetic, and citric acids did not yield very characteristic results, although a faint, hazy band at  $\lambda$  6800 was seen in several of these solutions. H. W.

#### **A New Electrometer for the Measurement of Radioactivity.**

B. SZILARD (*Anal. Fis. Quim.*, 1918, 16, 690—699).—A detailed description of a new improved electrometer of the attracted aluminium needle type especially adapted for radioactive measurements.

W. S. M.

#### **Radioactivity of some Canadian Mineral Springs.**

J. SATTERLY and R. T. ELWORTHY (*Trans. Roy. Soc. Canada*, 1917—1918, [iii], 11, 17—26).—The water of some sixty mineral



springs has been examined with respect to its content of radium emanation and dissolved radium. Measurements of the rate of flow and temperature of the water are also given, together with the nature of the strata. The emanation content varies from  $11.2 \times 10^{-12}$  curies per litre to  $345 \times 10^{-12}$  curies. The dissolved radium varies between the merest trace and  $46 \times 10^{-12}$  gram per litre, although in most cases the amount is very small. A tabular comparison is given between the factors for these springs and those of American and European springs. Thermal springs are shown to be more active than the cold springs. J. F. S.

**The Radioactivity of Mud from Rockanje.** E. H. BÜCHNER (*Chem. Weekblad*, 1918, 15, 243—246).—Examinations of samples of mud from the Waal lake, near Rockanje (A., 1913, ii, 221), showed proportions of radium of the order of  $1 \times 10^{-10}$  parts by weight. Subsequent examination in the following year confirmed this figure. More recent work on samples of the same material by Folmer and Blaauw (A., 1918, ii, 145) indicate a radium content of the order generally found in common rocks and deposits, namely,  $1 \times 10^{-12}$ . The author has examined some of the samples tested by Folmer and Blaauw, and confirms their results. The discordance between the later figures and the earlier results cannot be attributed to differences in the methods of working or to experimental error, but is possibly due to deposition from the river water in isolated places of matter containing a high proportion of some uranium mineral or its degradation products. S. I. L.

**The Radioactivity of the Mud from Rockanje.** A. H. BLAAUW (*Chem. Weekblad*, 1918, 15, 361—364).—Büchner's arguments (preceding abstract) to account for the differences shown by the later analyses in the radioactivity of the Rockanje deposits are criticised, and the assumptions of patches of higher activity questioned. Other geological arguments suggested by Büchner are shown to be incorrect. It is claimed that the later examination was complete. S. I. L.

**Ionisation and Resonance Potential for Electrons in Vapours of Magnesium and Thallium.** PAUL D. FOOTK and FRED L. MOHLER (*Phil. Mag.*, 1919, [vi], 37, 33—50).—The ionisation and resonance potentials for electrons in vapours of magnesium and thallium have been measured by the Tate modification of the Franck and Hertz method. The experimental values for magnesium vapour were 2.65 volts and 7.75 volts for the resonance and ionisation potentials respectively. The values calculated from the quantum relation  $h\nu = eV$  are 2.70 volts and 7.61 volts respectively. In the case of thallium vapour, the values 1.07 volts and 7.3 volts were obtained for the resonance and ionisation potentials respectively. The theoretical value for the former quantity is 1.07 volts, whilst that of the latter is unknown. The ionisation potential for magnesium is obtained from the limit of

the combination series  $1.5S - mp_2$ , and the resonance potential is determined by the first line in this series,  $m=2$ . In the case of thallium, the resonance potential is determined by the shorter wave-length member of the first term of the principal series of doublets. No known series in thallium has a convergence frequency greater than 49,263. The observed ionisation potential for thallium suggests the presence of an undiscovered series of single lines converging at  $\nu=1.5S=57,000$  to 60,000. The present work offers evidence that the single line spectra of magnesium and thallium are  $\lambda=4571$  and  $11,513$  Å. respectively. The general behaviour of the metals as regards ionisation and resonance potentials appears to be identical for metals in the same group of the periodic table. In the case of thallium, the component of the doublet having the higher frequency determines the value of the energy quantum absorbed by the atom. This fact suggests either the possibility of separate excitation of the components of a doublet by electronic impact or a behaviour of thallium vapour, thus excited, analogous to the emission of characteristic X-rays, for which the K group does not appear until the energy of the impacting electrons is greater than that corresponding with  $K_\gamma$ . The authors have obtained a value of Planck's constant,  $h$ , by the method of ionisation and resonance potentials. Using thirteen determinations on seven different metals, the final mean value  $h=6.55 \times 10^{-27}$  erg. sec. was obtained, which is in excellent agreement with recent determinations by other methods. The question of photoelectric sensibility of metallic vapours has been briefly discussed, and recent work on ionisation and resonance potentials has been considered critically.

J. F. S.

**The Emission of Positive Electricity by Salts of the Alkalies and Alkaline Earths under the Influence of Canal Rays.**

W. VÖLKER (*Ann. Physik*, 1918, [iv], 57, 257—277).—It is shown that when a suitably prepared thin layer of lithium chloride or of calcium sulphate, connected with a conducting system, is subjected to bombardment by canal rays, the induced currents can only be explained on the assumption that, when the cathode fall of potential exceeds a certain limiting value, positive charges are emitted by the salt. The limiting value of the cathode fall in the case of lithium chloride is about 500 volts, and with calcium sulphate about 1500 volts. These values correspond with the limiting values found by Stark and Wendt (*A.*, 1912, ii, 720), above which these salts, under the influence of canal rays, emit the characteristic metallic series lines. It is concluded that the carriers which emit the series lines, which are only observed in the space immediately adjacent to the salt, are the positive ions of the metallic elements themselves.

E. H. R.

**Measurement of Concentration of Hydrogen Ions and a New Form of Calomel Electrode.** W. STURM (*Chem. Weekblad*, 1918, 15, 912—916).—The author has designed a

hydrogen electrode which reaches equilibrium in about five minutes. This consists of a flask fitted with a rubber stopper pierced with three holes. The electrode, which passes through one of the holes, consists of a glass tube open at its lower end, and is surrounded by a cylinder of platinum gauze. An inner tube carries a copper wire connected to the platinum gauze by means of mercury, and a platinum wire. Hydrogen enters through a tube in the second hole, passes up the electrode, and escapes through a side-tube. The third opening carries a thermometer. The arrangement has the advantage that the fluid is throughout agitated in contact with the hydrogen, which results in a rapid equilibrium. The disadvantage, however, is that a considerable volume of fluid is required. Oxygen is removed from the hydrogen by means of heated platinised asbestos; the presence of small quantities of oxygen must be studiously avoided.

A form of calomel electrode is described in which mercury, mercury-calomel paste, potassium chloride crystals, and saturated potassium chloride solution are employed; such an apparatus has been in use for eight months satisfactorily.

S. I. L.

#### Electrolytic Conductivity in Non-aqueous Solutions. II. Electrical Conductivity of *p*-Tolyltrimethylammonium Iodide in Water and several Organic Solvents. HENRY

JERMAIN MAUDE CREIGHTON and D. HERBERT WAY (*J. Franklin Inst.*, 1918, **186**, 675—698. Compare *ibid.*, 1916, **182**, 745).—The electrical conductivity of *p*-tolyltrimethylammonium iodide has been determined at 25° in water, methyl alcohol, ethyl alcohol, propionaldehyde, anisaldehyde, benzaldehyde, acetone, formic acid, acetic acid, propionitrile, benzonitrile, nitromethane, nitrobenzene, and *epichlorohydrin*. In the case of some of the solvents, measurements have also been made at 0° and 18° and the temperature coefficient calculated. *p*-Tolyltrimethylammonium iodide, like most strong electrolytes, does not follow Ostwald's dilution law in aqueous solution, but is approximately in agreement with the Storch empirical dilution equation. The ionic conductivity of the *p*-tolyltrimethylammonium ion at 25° in aqueous solution is 40.3. The equivalent conductivity at infinite dilution has been extrapolated for *p*-tolyltrimethylammonium iodide in all the solvents used, and it is shown that the values vary from  $\Delta_{\infty} = 13$  in anisaldehyde to  $\Delta_{\infty} = 188$  in acetone. Further, the magnitude of this value bears a relationship to the chemical constitution of the solvent, which may be generally stated thus: the equivalent conductivity of an electrolyte at infinite dilution, and consequently the velocity of the ions, is greater in an aliphatic solvent than in an aromatic solvent of corresponding constitution. Thus  $\Delta_{\infty}$  for nitromethane = 115, for nitrobenzene 38; for propionitrile 143, whilst for benzonitrile  $\Delta_{\infty} = 54$ . In an homologous series, the value for  $\Delta_{\infty}$  is greater the nearer the solvent stands to the beginning of the series. For example,  $\Delta_{\infty}$  for water = 116, methyl alcohol 100, ethyl alcohol 48, formic acid 90, acetic acid 25. Of

the various substituting groups, the influence of the aldehyde group on the magnitude of  $\Delta_{\infty}$  is greatest, whilst that of the carboxyl group is the least, as is shown by the series: acetaldehyde  $\Delta_x = 188$ , nitromethane 115, methyl alcohol 100, acetic acid 25.

J. F. S.

#### Electrolytic Deposition of Iron from Organic Solvents.

E. H. ARCHIBALD and L. A. PIGUET (*Trans. Roy. Soc. Canada*, 1917—1918, [iii], 11, 107—112).—Solutions of ferric chloride in acetone, ethyl alcohol and acetone, and water and acetone, have been electrolysed by various currents and at various voltages at 25°. The experiments were carried out between platinum electrodes, but in some experiments a silver cathode was employed. In all cases, the iron can be completely deposited; in the case of acetone and of acetone-water mixtures, the iron is deposited free from carbon. At low voltages, the iron is deposited in the metallic condition; as the voltage is increased, it comes down as a red deposit which is adherent and allows the iron to be removed from the solution. From the acetone-alcohol solutions, the iron, although completely deposited, is contaminated with carbon. From acetone-water solutions of ferrous sulphate, the iron can be completely deposited, but the deposit contains a considerable amount of carbon. Aldehyde is not formed during the electrolysis of any of the solutions.

J. F. S.

#### Electrolytic Precipitation of Zinc.

D. MCINTOSH (*Trans. Roy. Soc. Canada*, 1917—18, [iii], 11, 113—119).—The electrolytic deposition of zinc from solutions of the sulphate has been studied under various conditions with the object of ascertaining the most suitable conditions for obtaining good deposits. It is shown that the best results are obtained when the solution is free from colloids and when the amount of iron present is low. The metals arsenic, antimony, copper, cobalt, nickel, and all metals more electropositive than zinc must be absent. The solution, particularly in tanks containing large amounts of acid, should be cold. The zinc deposits in a semi-passive form; but when it begins to dissolve, solution cannot be stopped in any simple way. The zinc concentration should be as high as possible (6—7%), and no attempt should be made to electrolyse solutions containing less than 1.5—2.0% of zinc. With the ordinary cascade system the maximum current density is 25—30 amperes per sq. foot. A large number of photographs of deposits obtained under varying conditions are reproduced in the paper.

J. F. S.

#### Critical Phenomena.

WILLIAM R. FIELDING (*Chem. News*, 918, 117, 379—383).—The relation between the critical pressure and critical temperature of an element can be expressed by the formula  $(T_c + 236.2)/\sqrt{P_c} = 70.9$ . This relation holds strictly for hydrogen and the members of the halogen group and less closely for nitrogen and xenon, whilst in the case of oxygen the divergence is considerable. For series of inorganic compounds such as that of the

halogen acids a similar formula holds,  $(T_c - x) / \sqrt{P_c} = k$ , where  $x$  and  $k$  are constants for any particular series. In inorganic compounds the critical pressure rises with the critical temperature in any series, but in organic compounds the pressure falls as the temperature rises. For a number of organic compounds the value of  $T_c \times \sqrt{P_c}$  has been calculated. In higher members of aliphatic series this quantity tends to become constant. In the aromatic series of hydrocarbons, with the introduction of alkyl groups into the benzene ring, it first decreases, and as the complexity of the alkyl groups increases it becomes practically constant. Multiplication of benzene rings in the molecule produces a considerable increase in the value of the quantity.

E. H. R.

**Calorimetric Lag.** WALTER P. WHITE (*J. Amer. Chem. Soc.*, 1918, **40**, 1858—1872).—Lags may pertain to the thermometer, to various portions of the calorimeter, or to outlying bodies, including air. In this paper the lag of external bodies, such as a thin metal shield surrounding the calorimeter, is treated in a mathematical manner. The effects prove to be three: one, equivalent to a change in the heat capacity of the calorimeter, which can be eliminated by direct calibration of the calorimeter; another, much smaller, depending on the amount of thermal leakage, which can be avoided by using the adiabatic method; and a third, dependent on the jacket temperature, which disappears if this is constant.

On account of the lag effect, the effective heat capacity of a shield midway between calorimeter and jacket is only one-fourth its actual capacity, and, with due regard to the possibility of change, such shields may often be used to reduce thermal leakage. Used as a cover, such a shield has a specially small error, and offers a particularly easy method of dealing with evaporation. (Compare A., 1918, ii, 149.)

E. H. R.

**The Conditions of Calorimetric Precision.** WALTER P. WHITE (*J. Amer. Chem. Soc.*, 1918, **40**, 1872—1886).—In a calibrated calorimeter most of the errors arise in thermometric measurements, and most of these come in the "cooling correction," the determination of the effect of thermal leakage. The leakage effect is equal to  $K\phi_z T$ , where  $T$  is the time,  $\phi_z$  is the difference between calorimeter and environment temperature, and  $K$  the leakage modulus of the calorimeter. By diminishing  $K$ , as by means of a vacuum, the effect of errors in  $\phi_z$  is diminished. These errors arise from the difficulty in getting the jacket and calorimeter temperatures uniform. The advantage of diminishing  $\phi_z$ , the thermal head, is largely illusory, since the main error, that in determining  $K$  by means of the cooling rate, is little affected. Lags, which vary with  $K$  and are independent of  $T$  and  $\phi$ , can be made to cause little or no error. The rate of stirring should be as uniform as possible, since the heat produced varies as the cube of the speed. The type of stirrer and design of the calorimeter with reference to stirring may be important.

E. H. R.

**Calorimetric Methods and Devices.** WALTER P. WHITE (*J. Amer. Chem. Soc.*, 1918, **40**, 1887—1898).—The general rules for calorimetric precision (preceding abstract) are applied to jacket covers and stirrers and to such special devices as vacuum-jacketed vessels, the adiabatic method, aneroid or dry calorimeters, double or differential calorimeters, and measured-shield calorimeters, and the advantages of the different forms of calorimeter are compared. The measured-shield calorimeter is a new device, having between the calorimeter and the jacket a thin metal shield connected to the wall of the jacket by thermo-elements which are used to measure the thermal head.

E. H. R.

**Sensitive Bath Thermostat.** A. NORMAN SHAW (*Trans. Roy. Soc. Canada*, 1917—18, [iii], **11**, 129—135).—A thermostat on a rather large scale is described which differs but little from the well-known types. A note on the regulation of temperature is appended to the paper.

J. F. S.

**An Accurate Method for Measuring the Density of Gases.** O. MAASS and J. RUSSELL (*J. Amer. Chem. Soc.*, 1918, **40**, 1847—1852).—The method described is applicable to the determination of the density of those gases which can be condensed by liquid air or some other freezing agent. The purified, dry gas is condensed in a suitable vessel, and thence transferred to a large exhausted glass flask (about 2½ litres capacity) the volume of which is accurately known. The flask has a connection to a manometer, and the pressure is read at 0°, the flask being immersed in ice. By a suitable arrangement of tubes the gas in the flask can be transferred to an exhausted glass bulb immersed in liquid air. When the gas has liquefied, the bulb is sealed off and weighed, and again weighed after it has been opened and the liquid allowed to evaporate. The pressure of the gas remaining in the flask and connecting tubes is read after the bulb has been detached, to enable the volume of gas taken into the bulb to be calculated. The accuracy of the method is limited by the accuracy with which the height of the mercury in the manometer can be read. The probable error with the method used is 0.05%; with the aid of a cathetometer it could be reduced to 0.01%.

The following densities were determined: acetylene, 1.1695; methyl ether, 2.1103; hydrogen bromide, 3.6397.

E. H. R.

**The Change of Density of Liquid Mixtures with Increasing Temperature.** W. HERZ (*Zeitsch. anorg. Chem.*, 1918, **104**, 251—252).—The formula expressing the relationship between density and temperature,  $1/d_t = a - b \log(\theta - t)$ , where  $d_t$  is the density at temperature  $t$ ,  $\theta$  is the critical temperature, and  $a$  and  $b$  are constants, has been found to hold for liquid mixtures as well as for pure liquids. Different binary mixtures of benzene, toluene, aniline, and nitrobenzene were used for the experiments, at temperatures between 25° and 90°, and the differences between observed and calculated densities were very small.

The critical temperature  $\theta$  of the mixture was calculated from those of the constituents,  $\theta_1$  and  $\theta_2$ , by means of the formula  $\theta = n\theta_1 + (100 - n)\theta_2/100$ , where  $n$  and  $(100 - n)$  are the percentages of each constituent.

E. H. R.

**Molecular Attraction and Attraction of Mass, and some New Gas Equations.** JAMES KAM (*Phil. Mag.*, 1919, [vi], 37, 65—97).—A theoretical paper, in which gas equations are deduced from considerations of the actual and theoretical co-volumes. A general equation is deduced which considers the effect of temperature on the relation of the co-volumes to the volume. Further reduced isothermals and reduced border-curves are considered. It is shown that the cohesive forces causing the "inward pressure" appear to follow a law similar to the inverse square law of mass attraction. From the deviations from the gas laws a value for the tensile strength of iron is deduced which is of the same order as the experimental value. It is further shown that whatever the ultimate nature of the cohesive forces may be, they seem to be proportional to the square of the molecular weight and to obey the inverse square law—a law consequently similar to Newton's law of attraction of mass.

J. F. S.

**Internal Molecular Forces of Solid Substances and their Relations with the Elastic Properties.** STEFANO PAGLIANI (*Nuovo Cim.*, 1918, [vi], 15, i, 103—129).—The existence of three forms of internal molecular forces in solids is considered and their values calculated. The first,  $F$ , termed intermolecular force of coherence, enters as a factor in the internal work into which thermal or mechanical energy can be transformed without change in the volume of the substance. The second,  $\pi$ , termed internal pressure, is analogous in character to external pressure, and enters as a factor in the internal work in which thermal energy is used with variation of the volume of the substance. The third, called intermolecular force of change of phase, enters as a factor in the internal work accomplished during changes of phase—in the fusion of solids; this force, which acts at the temperature of fusion, where Lindemann considers that the amplitudes of the atomic oscillations about their equilibrium position become of the same order of magnitude as the mean distance between the atoms, appears to be of the same nature as  $F$ , which acts with definite values at different temperatures.

The magnitude of the force  $F$  exhibits relationships with the values of some of the magnitudes considered in the study and applications of the elastic properties of solids. The simplest of these relations with the moduli of elasticity of tension  $E$ , of rigidity  $n$ , and of flow  $N$  are as follows:  $E = 1.70 F$  or approximately  $E = 5F/3$ ,  $n = F/\pi$ , and  $N = 2F/\pi$ . The relatively great value of the ratio between  $E$  and  $F$  depends on the fact that the load  $E$ , which should double the initial length of the solid, is only an ideal load unattainable in practice. It is hence more accurate to replace  $E$  in technical formulae by  $F$ , this being a real magnitude the value

of which at different temperatures may be calculated by means of physical magnitudes exactly measurable; a number of expressions are given in which this substitution is made. The modulus of elasticity for each species of deformation is found to be directly proportional to the molecular force of coherence. T. H. P.

#### The Adsorption of Arsenious Acid by Ferric Hydroxide.

MAITLAND C. BOSWELL and J. V. DICKSON (*J. Amer. Chem. Soc.*, 1918, **40**, 1793—1801).—The adsorption of arsenious acid from solution, by ferric hydroxide which had been prepared several months previously, has been studied both in presence and absence of sodium hydroxide. The adsorption of the arsenious acid by the ferric hydroxide is diminished by the presence of sodium hydroxide, whilst the adsorption of the sodium hydroxide is itself increased by the presence of the arsenious acid. The age of the ferric hydroxide and the addition of sodium chloride appear not to have any effect on the quantitative data recorded.

The results follow only approximately the "adsorption law,"  $E = \beta A^p$ , where  $E$  is the concentration of the adsorbed substance in the adsorbing phase,  $A$  its concentration in the solution at equilibrium, and  $\beta$  and  $p$  are constants. The equation can be written  $\log E = p \log A + B$ . Hence if the logarithms of the concentrations in the adsorbent and the solution be plotted, a straight line should be obtained, the slope of which gives the value of  $p$  whilst the intercept gives the value of  $B = \log \beta$ . The curves thus obtained from the results of the authors' experiments approximate to straight lines, but all show a distinct concavity to the  $x$  or  $\log A$  axis. The adsorption phenomenon cannot be exactly represented by the above equation. The adsorption of arsenious acid by ferric hydroxide was also studied by Mecklenburg (*A.*, 1913, ii, 676), who concluded that the adsorption curves for any particular gel prepared under varying conditions are so related to a unit curve that the ratio of any ordinate on one curve to the corresponding ordinate on the unit curve is a constant. The authors interpret this to mean that the exponent  $p$  in the equation  $E = \beta A^p$  is constant for any particular gel, whilst  $\beta$  is a variable depending on the conditions of preparation of the gel. The values of  $p$  calculated from the authors' and Mecklenburg's results agree when arsenious acid is used alone, but in presence of sodium hydroxide its value increases. E. H. R.

#### Ferment Action. II. Adsorption of Amino-acids and Polypeptides by Animal Charcoal. Relation of the Observed Appearances to the Cleavage of Polypeptides by Yeast Juice.

ERIL ABERHALDEN and ANDOR FÖDÖR (*Fermentforsch.*, 1917, **2**, 74—102; from *Chem. Zentr.*, 1918, ii, 738. Compare *A.*, 1917, i, 306).—Animal charcoal adsorbs scarcely a trace of glycine, but it adsorbs a little alanine and a comparatively large quantity of leucine. Similar variations are observed in the case of the polypeptides, even isomeric substances being adsorbed to very different extents by the charcoal. The amount adsorbed at various dilutions



varies according to the laws of adsorption, just as has been observed in the case of enzymes. The adsorptive power of charcoal differs from that of the enzymes, however, in being uninfluenced by changes in the concentration of the hydrogen and hydroxyl ions in the solution.

When mixtures of amino-acids or polypeptides are treated with animal charcoal, the adsorption of the substances containing the more complex molecules is relatively increased, whilst that of smaller molecular substances is decreased. H. W. B.

**Ferment Action. III. Adsorption of Amino-acids and Polypeptides and also of various Carbohydrates by Animal Charcoal.** EMIL ABDERHALDEN and ANDOR FODOR (*Fermentforsch.*, 1917, 2, 151—166; from *Chem. Zentr.*, 1918, ii, 739. Compare preceding abstract).—*L*-Arabinose, levulose, and inositol are less readily adsorbed by charcoal than dextrose, sucrose, and other disaccharides and trisaccharides. The presence of carbohydrates diminishes the adsorptive power of animal charcoal towards polypeptides, and conversely the adsorption of carbohydrates is adversely influenced by polypeptides. H. W. B.

**Retardation by Sugars of Diffusion of Acids in Gels.** EVARTS A. GRAHAM and HELEN TREDWAY GRAHAM (*J. Amer. Chem. Soc.*, 1918, 40, 1900—1917).—The rates of diffusion of a number of inorganic and organic acids into gelatin solutions containing varying amounts of dextrose, sucrose, and lactose have been measured. All the sugars have a marked retarding influence on the diffusion of any acid, the disaccharides having a considerably greater effect than the monosaccharide. In agreement with the general diffusion law, the ratio of the distance of diffusion to the square root of the time is found to be a constant in gelatin both with and without sugar. The retardation is not proportional to the concentration of the sugar, but is relatively greater for smaller concentrations of sugar. If the ratio  $d/\sqrt{t}$  is equal to  $K_0$  without sugar and  $K$  with sugar, the relative retardation is given by  $(K_0 - K)/K_0$  or  $\Delta/K_0$ . The relation between concentration of sugar and retardation can be expressed approximately by the equation  $(\Delta/K_0)^n = ac$ , where  $c$  is the concentration and  $a$  and  $n$  are constants. In 10% gelatin, nitric acid behaves abnormally in that the ratio  $d/\sqrt{t}$  is not constant, but increases rapidly at first and, after remaining constant for some time, again decreases. Hydrochloric acid shows the same behaviour in 3% gelatin.

Sodium chloride also retards the diffusion of acids into gelatin, but to a less extent than the sugars when equimolecular solutions are compared. This is the reverse of their effect in reducing the acid swelling of gelatin, in which sodium chloride is more effective than sugar. The physiological bearing of the results obtained is briefly discussed, particularly with reference to the protective action of dextrose in cases of chloroform poisoning, the effects of

which are ascribed to the presence of free hydrochloric acid in the substance. The mechanism of the retardation is also discussed.

E. H. R.

**Chemical Affinity in Crystals and the Velocity of Crystallisation.** M. PADOA (*Atti R. Accad. Lincei*, 1918, [v], 27, ii, 59—64; *Gazzetta*, 1918, 48, ii, 139—147).—The suggestion is made that, in most cases, crystallisation represents a transposition effected by means of valencies among the more or less free molecules of the gaseous or liquid phase, so that velocity of crystallisation may be regarded as velocity of reaction. The author has measured the velocities of crystallisation of a number of super-cooled compounds with the object of ascertaining: (1) if, with isomorphous compounds of similar structure, the velocities of crystallisation are equal or of the same order of magnitude, and (2) if, in a series of compounds of perfectly analogous chemical constitutions, the velocities of crystallisation are comparable and, *ceteris paribus*, dependent on the molecular weights. Similar values are obtained for *m*-bromo- (600) and *m*-chloro-nitrobenzene (882), and also for *p*-dichloro- (4800), *p*-dibromo- (7000), and *p*-iodo-benzene (6000), the low value for *p*-chloriodobenzene (1153) being apparently dependent on its markedly different viscosity. The introduction of methyl into the benzene ring greatly retards the crystallisation; naphthalene and its analogues show far lower values than benzene, the isomeric anthracene and phenanthrene having identical velocities. Similarity also exists between the velocities for isomorphous inorganic compounds.

Of two compounds of similar structure, the one saturated and the other unsaturated, the latter should present the greater velocity of crystallisation, since the latent affinities in the double linkings would favour the process of crystallisation. This conclusion is completely confirmed by the results obtained for a number of pairs of isomorphous organic compounds, one member of each pair being saturated or at least less unsaturated than the other member.

The general conclusions drawn are: (1) the velocity of crystallisation is a constitutive property, and (2) the bonds between the atoms in crystalline networks are of the same nature as chemical valencies.

T. H. P.

**Point of Transformation between Reversible Modifications.** C. VIOLA (*Atti R. Accad. Lincei*, 1918, [v], 27, ii, 107—112).—The author applies the law of maximum work and Curie's law to the consideration of the possible co-existence, at a temperature different from  $T'$ , of two reversible crystalline modifications which occur in contact in stable equilibrium at temperature  $T$  and at a definite pressure. It is shown that, either where a process is effected reversibly and crystallisation takes place and should take place according to Curie's law, or where between two modifications in contact a minimal surface tension is established, a point of

transformation must always exist there; vice versa, the surface tension is a minimum at a transformation point between two modifications.

T. H. P.

**The Artificial Coloration of Liquid Crystals.** PAUL GAUBERT (*Compt. rend.*, 1918, 167, 1073—1075).—Indophenol may be satisfactorily used for colouring liquid crystals and also solid crystals of a large number of organic compounds. The presence of the indophenol lowers the solidification point of the molten substances, and in the case of substances giving several birefringent liquid phases, all the melting points or transformation points are lowered. There exists for the indophenol a coefficient of solubility particular to each phase, this coefficient diminishing with the molecular volume.

The optically positive liquid crystals obtained by combining cholesterol with glycollic acid, glycerol, etc., are not coloured by indophenol, although the isotropic liquid dissolves it. W. G.

**Theory of the Velocity of Coagulation.** H. FREUNDLICH (*Kolloid Zeitsch.*, 1918, 23, 163—173).—A theoretical paper in which it is shown that the velocity of slow coagulation of hydrophobe sols increases very much with increasing concentration of the coagulating electrolyte, whilst for rapidly coagulating sols the velocity of coagulation is constant and independent of the nature and concentration of the electrolyte. Smoluchowski explains the rapid coagulation by assuming that the collisions between the particles are non-elastic and lead to the coagulation of all the particles which come within the sphere of influence. The rapid increase in velocity of the slow coagulation is explained by the assumption that in the concentration present the charges on the particles produce a repulsion, and only those particles are coagulated the kinetic energy of which is greater than a certain critical value. This critical value is greater the greater the charge on the particle. The number of these particles increases as the electrolyte concentration increases. A formula giving the relationship between electrolyte concentration and velocity of coagulation is given, and this is in keeping with observed results. J. F. S.

**The Brownian Movement and the Coagulation of Colloidal Solutions.** H. W. WOUTSTRA (*Chem. Weekblad*, 1918, 15, 679—680).—The author claims priority over Kruyt and van der Spek (*A.*, 1917, ii, 563) in directing attention to the function of the Brownian movement of the colloid particles in the coagulation of a colloidal solution. W. S. M.

**The Brownian Movement in Relation to the Mechanism of Flocculation.** D. J. HISSINK (*Chem. Weekblad*, 1919, 16, 20—21).—The author disputes the contention of Henri and Ostwald (see "*Grundriss der allgemeinen Chemie*," 1917, 544) that the Brownian movements are diminished by addition of a coagu-

lating electrolyte before coagulation, and contends that by microscopic observation it can easily be seen that the coagulation itself is the cause of the diminution of the movement, which is therefore a consequence of the coagulation and does not precede it.

S. I. L.

**The Lowering of the Degree of Dissociation.** R. N. DE HAAS (*Chem. Weekblad*, 1918, 15, 1352—1355).—An elementary mathematical consideration of the fundamental equation of mass action with reference to the shifting of the equilibrium consequent on the addition of one of the products of dissociation or ionisation to the system.

W. S. M.

**Heterogeneous Equilibria between Aqueous and Metallic Solutions: The Interaction of Mixed Salt Solutions and Liquid Amalgams. V. A Study of the Ionisation Relations of Potassium and Strontium Chlorides in Mixtures.**

G. MCP. SMITH and EDWIN ARTHUR REES (*J. Amer. Chem. Soc.*, 1918, 40, 1802—1847).—To study the equilibrium between mixed strontium and potassium amalgams and the mixed aqueous solutions of the chlorides of these metals, a definite quantity of either strontium amalgam or potassium amalgam of known concentration was shaken up with successive portions of a known aqueous solution of the mixed chlorides until equilibrium was reached. The quantities of strontium and potassium in the amalgam were then determined by analysis. Experiments were made on the effect of varying (1) the amalgam concentration up to about 0.6 milliequivalent of potassium or strontium per 10 grams of mercury, (2) the total salt concentration in the aqueous phase from 0.05*N* to 3*N*, (3) the ratio of the two salts in the aqueous phase at different total salt concentrations, and (4) the temperature from 15° to 40°. To interpret the data obtained, the value of the expression  $(\text{Sr}_{\text{Hg}})(\text{K-salt})^2/(\text{K}_{\text{Hg}})^2(\text{Sr-salt})=C_c$  was calculated, in which  $(\text{Sr}_{\text{Hg}})$  and  $(\text{K}_{\text{Hg}})$  are the respective atom-fractions in the mercurial phase, and (K-salt) and (Sr-salt) are the mol-fractions in the aqueous phase (compare A., 1917, ii, 247). The value of the "equilibrium expression"  $C_c$  increases proportionately with the total concentration in the mercurial phase up to 0.3 milliequivalent per 10 grams of mercury, at temperatures from 15—45°. When the amalgam concentration is kept constant and the concentration of the aqueous phase increased, the proportions of the two salts being kept constant, the value of  $C_c$  first falls rapidly as the concentration rises to about 0.4*N*, but with stronger solutions it approaches a constant value.

Assuming that, in the most dilute solutions examined, 0.05*N*, an equimolecular mixture of the two salts is completely ionised, it is shown that, as the concentration in the aqueous phase is increased, but the salt ratio kept constant, the proportion of  $\text{K}^+$  ions to  $\text{Sr}^{++}$  ions increases rapidly; also when the ratio of

potassium chloride to strontium chloride is increased, the proportion of  $K^+$  ions increases at a greater rate.

The results obtained at different temperatures have been used to calculate the heat of reaction accompanying the changes between  $15^\circ$  and  $40^\circ$ . With rising temperature, the reaction is exothermic, and the heat of reaction is found to decrease with increasing total salt concentration.

As regards the dissociation of potassium and strontium amalgams, it is shown that the ordinary mass-action expression holds good for mixtures of the two up to a total concentration of about 2 milli-equivalents per 100 grams of mercury. There is evidence of the formation in the aqueous salt mixture of molecular complexes and complex ions, the results being in harmony with Werner's views.

E. H. R.

**Influence of Substitution of the Components of Binary Equilibria in Solution. XIII. The Solution Equilibria of the Three Isomeric Phenylenediamines with Phenols and the Dinitro-derivatives of Benzene respectively.**

ROBERT KREMANN and WOLFGANG STROHSCHNEIDER (*Monatsh.*, 1918, **39**, 505—570. Compare this vol., ii, 15).—Melting-point and cooling curves have been obtained for the six binary systems made up of the three phenylenediamines with either  $\alpha$ -naphthol or  $\beta$ -naphthol, for the four binary systems composed of  $\alpha$ - or  $\beta$ -naphthol with  $\alpha$ - or  $\beta$ -naphthylamine, for the system  $\beta$ -naphthol and *p*-toluidine, for the nine binary systems composed of one of the three diphenylamines with one of the three dihydroxybenzenes, for the three binary systems composed of 2:4-dinitrotoluene with each of the phenylenediamines, and for the nine binary systems composed of one of the three phenylenediamines with one of the dinitrobenzenes. The results are given in curves and in voluminous tables. It is shown that *p*-phenylenediamine forms compounds with two molecules of  $\alpha$ -naphthol (m. p.  $110^\circ$ ) and with two molecules of  $\beta$ -naphthol (m. p.  $150.5^\circ$ ). One molecule of *m*-phenylenediamine forms compounds with two molecules of  $\beta$ -naphthol (m. p.  $114^\circ$ ) and with one molecule of  $\alpha$ -naphthol (m. p.  $35^\circ$ ). One molecule of *o*-phenylenediamine forms compounds with one molecule of  $\alpha$ -naphthol (m. p.  $60^\circ$ ) and with one molecule of  $\beta$ -naphthol (m. p.  $86^\circ$ ) respectively.  $\alpha$ -Naphthol forms two compounds with  $\alpha$ -naphthylamine with one and four molecules of the latter to one of the former compound. A compound is formed containing two molecules of  $\beta$ -naphthol to three molecules of  $\alpha$ -naphthylamine, but no compounds are formed between  $\alpha$ -naphthol and  $\beta$ -naphthylamine; a simple eutectic is produced by these substances at  $47^\circ$ , and contains 56.5% of the last-named component. An equimolecular compound is formed between  $\beta$ -naphthol and *p*-toluidine (m. p.  $87.5^\circ$ ). Equimolecular compounds are formed with *m*-phenylenediamine and catechol (m. p.  $64.5^\circ$ ), *m*-phenylenediamine and resorcinol (m. p.  $79^\circ$ ), *m*-phenylenediamine and quinol (m. p.  $127^\circ$ ), with two molecules of catechol and one mole-

cule of *p*-phenylenediamine, with three molecules of catechol and two molecules of *p*-phenylenediamine, and with three molecules of quinol with one molecule of *p*-phenylenediamine. The details of the system *o*-dinitrobenzene-*p*-phenylenediamine have not been worked out, because of a secondary chemical reaction which interferes with the measurements. Compounds are formed between *m*-dinitrobenzene and the three phenylenediamines of the following composition: (i) three molecules of the nitro-compound with two molecules of *o*-phenylenediamine, (ii) two molecules of the nitro-compound with one molecule of *o*-phenylenediamine, and (iii) one molecule of the nitro-compound with two molecules of *m*-phenylenediamine; no compounds are formed between *p*-phenylenediamine and *m*-dinitrobenzene. In the case of *p*-dinitrobenzene and the three phenylenediamines, compounds are not formed with *o*- and *m*-phenylenediamine, but with *p*-phenylenediamine, a compound of two molecules of the amine and one molecule of the nitro-compound is formed. Full details of the numerous eutectics are given in the paper.

J. F. S.

**The Dilution Limits of Inflammability of Gaseous Mixtures. III. The Lower Limits of some Mixed Inflammable Gases with Air. IV. The Upper Limits of some Gases, Singly and Mixed, in Air.** HUBERT FRANK COWARD, CHARLES WILLIAM CARPENTER, and WILLIAM PAYMAN (T., 1919, 115, 27—36).

**The Propagation of Flame through Tubes of Small Diameter. II.** WILLIAM PAYMAN and RICHARD VERNON WHEELER (T., 1919, 115, 36—45).

**The Inflammation of Mixtures of Ethane and Air in a Closed Vessel. The Effects of Turbulence.** RICHARD VERNON WHEELER (T., 1919, 115, 81—94).

**The Ignition of Explosive Gases by Electric Sparks.** JOHN DAVID MORGAN (T., 1919, 115, 94—104).

**The Range of Existence of Substances, Kinetic Analysis, and the Estimation of Vapour Pressures from Reaction Velocities.** M. TRAUTZ (*Zeitsch. anorg. Chem.*, 1918, 104, 169—210).—The author distinguishes between the range of stability and the range of existence of any substance. The stability of a substance is dependent on the chemical factors which bring about its formation, and is measured by the energy of the reaction, whilst its range of existence is determined only by the heat of activation needed to bring about its decomposition. The upper limit of existence of a compound is determined by the heat of activation of that binary decomposition which requires the least energy.

From the point of view of the author's theory of reaction velocity (A., 1917, ii, 23; 1918, ii, 151), a large number of reactions are

discussed. The formation of nitrosyl chloride or of nitrosyl bromide is apparently a reaction of the third order, but in all probability is made up of superimposed reactions of lower orders, and formulæ are developed by means of which the higher order reaction can be expressed in terms of reactions of lower orders. On the assumption that nitrosyl chloride formation proceeds in the two stages  $\text{NO} + \text{Cl}_2 = \text{NOCl}_2$ ,  $\text{NOCl}_2 + \text{NO} = 2\text{NOCl}$ , a method of kinetic analysis is developed which enables the concentration and heat of formation of the intermediate product to be calculated. The heat of formation of  $\text{NOCl}_2$  is 2500 cal.

The reaction between hydrogen and oxygen in porcelain vessels was supposed by Bodenstein to be of the third order, but the velocity constants do not distinguish between a third- and a second-order reaction. Moreover, probable values for the impact constant are obtained only if it is treated as a second-order reaction. The course of the reaction is probably  $\text{H}_2 + \text{O}_2 = \text{H}_2\text{O}_2$  (measurable);  $\text{H}_2\text{O}_2 + \text{H}_2 = 2\text{H}_2\text{O}$  (immeasurably fast). The probable value of the heat of activation for  $\text{H}_2 + \text{O}_2$  is 46,374 cal., and the mean diameter of oxygen and hydrogen molecules,  $1.62 \times 10^{-8}$  cm.

The formation of nickel carbonyl from nickel and carbon monoxide, which is apparently a third-order reaction, probably proceeds in the three stages:  $\text{Ni} + \text{CO} = \text{NiCO}$  (momentary equilibrium),  $\text{NiCO} + \text{CO} = \text{Ni}(\text{CO})_2$  (measurable), and  $\text{Ni}(\text{CO})_2 + 2\text{CO} = \text{Ni}(\text{CO})_4$  (immeasurably fast). It is shown how, from the velocity of the reaction, the vapour pressure of nickel can be calculated, and also its probable boiling point, 3358° A.T. The true order of a reaction, for example, in the case of nickel carbonyl formation, can be determined by consideration of the absolute reaction velocity and its temperature coefficient when the mean molecular diameter is assumed.

The velocity of surface reactions is fully discussed, and in this connexion the decomposition of ammonia, phosphine, arsine, and antimony hydride are considered. These reactions are assumed to be of the first order, corresponding with  $\text{XH}_3 \rightarrow \text{XH} + \text{H}_2$  (measurable). The heat of activation in this series decreases with increasing molecular weight. From the heat of activation, the maximum wave-length of the actinic rays which will bring about the decomposition is calculated from the formula

$$q_0 = (2.843 \times 10^7) / \lambda.$$

It is concluded that ammonia, phosphine, and arsine should show absorption in the ultra-violet, antimony hydride in the visible spectrum. For ammonia, the maximum wave-length is shown to be 219.6  $\mu$ , and in confirmation of this, it is shown experimentally that light of 214–203  $\mu$  is photochemically active towards ammonia.

Other reactions discussed are the formation and decomposition of sulphuryl chloride, the decomposition of sulphur trioxide and hydrogen selenide, the formation of hydrogen sulphide and hydrogen selenide from their elements, and the slow combustion of hydrogen iodide, of phosphorus, sulphur, and carbon. From Rhead

and Wheeler's experiments on the combustion of carbon to carbon monoxide (T., 1912, 101, 846), assuming that the vapour of carbon is monatomic, the boiling point of carbon is calculated to be  $3542^{\circ}$  and its vapour pressure in mm. of mercury at  $1100^{\circ}$ ,  $4.05 \times 10^{-9}$ , the corresponding concentration being  $4.74 \times 10^{-14}$  mols. per litre.

E. H. R.

**Consecutive Reactions. IV. Relationships of the Constants in the Acid Hydrolysis of Esters of Oxalic and Malonic Acids.** ANTON SKRABAL and (Frl.) DANICA MRAZEK (*Monatsh.*, 1918, 39, 495—503. Compare A., 1917, ii, 250).—The kinetics of the acid hydrolysis of methyl oxalate, ethyl oxalate, methyl malonate, and ethyl malonate have been studied at  $25^{\circ}$ . The hydrolysis was effected by 0.1N-hydrochloric acid, and since, as has been previously shown, the determination of the change in acidity did not yield a satisfactory constant, the amount of normal ester remaining unchanged was determined iodometrically. In this way, it is shown that the hydrolysis takes place according to the equations for first-order reactions. The ratio of the reaction constants of the two consecutive reactions is 2:1. Methyl oxalate is hydrolysed approximately twice as rapidly as ethyl oxalate, but in the case of the malonic esters, the rate of hydrolysis is approximately the same in the two cases.

J. F. S.

**The Conception of the Chemical Element as Enlarged by the Study of Radioactive Change.** FREDERICK SODDY (T., 1919, 115, 1—26).

**Atomic Weights in 1917.** E. MOLES (*Anal. Fis. Quim.*, 1918, 16, 625—653).—A review of the work on the determination of atomic weights published during 1917.

**Complex Ions.** I. M. KOLTHOFF (*Chem. Weekblad*, 1918, 15, 1636—1644).—The definitions of complex ions given by de Haas (*ibid.*, 1917, 14, 752; 1918, 15, 1352) and Abegg and Bodländer (A., 1899, ii, 542) are criticised. The latter state: "One of the ion-forming components of a complex compound is built up of a single ion with an electrically neutral molecule." de Haas in his later paper defines an inorganic complex ion as "a metal-containing ion built up of one or more molecules and one or more ions." The author does not regard the presence of a neutral molecule as essential. Complex ions arise from the tendency of ions to combine with other molecules or ions, which tendency is the greater the lower is the "electro-affinity" of the ion; the nature of the complex is dependent also on the properties of the molecules or other ions which enter into it. It follows that for any salt, formation of complex ions becomes important only when neutral molecules are present to enter into combination with the ions, that is, when the degree of dissociation is small. Thus salts of strongly electropositive and electronegative ions or groups, and salts of one



strong and one weak radicle, being highly dissociated in solution, show small tendency to complex formation; salts of one strong and one weak radicle or element may, however, form complex ions by combination of the ions of the weaker element or radicle with each other.

The mercuric salts afford numerous examples of the formation of complex ions; dissociation of mercuric chloride forms the ions  $\text{HgCl}'$ ,  $\text{Hg}''$ , and  $\text{Cl}'$ , and combination of the  $\text{Cl}'$  with the undissociated molecule gives rise to the complexes  $\text{HgCl}_3'$  and  $\text{HgCl}_4'$ . Of these, the group  $\text{HgCl}'$  has the highest concentration, namely, about 10,000 times as great as the concentration of the  $\text{Hg}''$  ion. A consideration of the possibilities of combination or dissociation of a group  $\text{AB}'$ , where A is a bivalent positive and B a univalent negative ionogen, will show that the neutral molecule  $\text{AB}_2$  can be regarded as an intermediate product between the complexes  $\text{AB}'$  and  $\text{AB}_3'$ .

The cases of formation of complexes fall into two classes. In the first, the electro-affinity of both ions is great, and the tendency to complex formation small, increasing as the electro-affinity falls. In the case of the chlorides of the alkali metals in solution in presence of an alkaline earth chloride, for example, the lower dissociation of the alkaline earth chloride causes the presence of its neutral molecules, which form complexes with the chlorine ion of the alkali metal chloride, of the type  $\text{RCl}_3'$ ; in concentrated solutions, the product of the concentration of this complex and that of the ion of the alkali metal may be so great as to cause separation of double salts. In the second class, the electro-affinity of both ions is small; it is clear that there will be a gradual transition between the two classes. Silver iodide and mercuric cyanide form examples of slightly soluble salts in this class; here the solubility is greatly increased by presence of either ion, owing to the possibility of complex formation which this introduces. Cadmium iodide affords a good case of a soluble salt of this class.

Consideration is given to complex ions containing hydrogen. For the case of a weak dibasic acid,  $\text{H}_2\text{A}$ , two dissociation constants, corresponding with the ions  $\text{HA}'$  and  $\text{A}''$ , have to be considered, the second being usually very small. It is shown that the low dissociation of  $\text{HA}'$  as compared, for example, with  $\text{RA}'$ , where R is an alkali metal, is in contrast with the case of the halogen acids and the alkali haloids, the former having here the higher dissociation.

The following definition is finally put forward: "Complex ions break up to a certain extent into simple ions, generally with formation of neutral molecules." S. I. L.

**The Valency-hypothesis of J. Stark.** W. JACOBS (*Chem. Weekblad*, 1918, 15, 1566—1571).—The theory of partial valencies has been employed to explain molecular aggregation in the fluid and crystalline states and to account for the various states of aggregation in which elements and compounds exist at ordinary

temperatures, and the changes in the states of aggregation which they undergo with change of temperature. The lines of force of a valency-electron can be distributed partly to atoms of the same molecule and partly to other molecules; consequently, intramolecular linking and intermolecular linkings are essentially due to the same forces, and all substances fall within a series in which the relative strength of the two classes of linking gradually changes. If the valency-electron is adjacent to a positive surface within its own molecule, intermolecular attraction will be weak and will be easily overcome by a small inflow of energy from without, which will leave the intramolecular system unchanged; at the other extreme, the strength of the two kinds of linkings approaches equality, the molecule behaves, as it were, like a single atom, and intermolecular aggregation is pronounced. In the last case, any disturbance of the intermolecular linkings must affect strongly the internal arrangement of the single molecules, and it may happen that a particular atomic system can only exist within very narrow limits of physical properties.

Stark has directed attention to the distinction between the meaning of the term molecule in the chemical and in the physical sense; in the former, molecules are distinguished as having identical arrangements of atoms, in the latter as being particles free to move in space in a definite manner determined by thermal conditions. The two definitions agree for molecules in the gaseous condition, since here no intermolecular linkings exist. In the crystalline condition, a chemical molecule is not free to move independently of its neighbours, and the physical definition fails. In the liquid condition, molecular aggregation occurs, but generally varies continually in strength and character; physical molecules exist, but are generally not identical with chemical molecules, being usually built up of several chemical molecules and varying continually in mass. In the case of solution, the molecules of solute by the attraction of their partial valencies form "solution molecules" with molecules of the solvent, each of which is a free-moving physical molecule and changes readily with slight changes of temperature.

Where intramolecular attraction is weak and the electric valency-field is diffused outside the molecule, as in the case of metals and electrolytes, the power of crystallisation is high, and in the liquid condition the substance has low vapour pressure; where the intramolecular linkings are very strong, as with the inert gases, the substance cannot be liquefied or solidified at ordinary temperatures. The gradation of physical properties of the hydrocarbons similarly is explained by the gradual decrease of strength of the intramolecular bonds as the number of similarly linked atoms within the molecule increases.

S. I. L.

**A Device for Introducing a Vapour into a Gas.** E. H. ZEITZUCHS (*J. Amer. Chem. Soc.*, 1918, **40**, 1899).—To introduce a known quantity of vapour into a stream of gas, the following

device is used. On to the end of a burette is sealed a glass capillary. This capillary is enclosed by the constricted end of a wide tube, closed at the top just below the cock of the burette by a piece of rubber tubing, which keeps it in position. The capillary touches in the wide tube a roll of asbestos fibres, wound round with resistance wire, by which it is heated electrically. A measured quantity of liquid can be run from the burette on to the asbestos fibre, where it is vaporised and taken up by a stream of gas entering the constricted portion of the tube by a side-tube and passing down through the asbestos roll. Any known quantity of vapour can thus be introduced into the gas.

E. H. R.

**Stopcock for Dropping Liquids arranged for Equalising the Pressure Above and Below the Outlet in the Stopcock.**

HARRY L. FISHER (*J. Ind. Eng. Chem.*, 1918, 10, 1014—1015).

An annular groove is provided in the key of the stopcock and a central tube is fitted in the two arms. The groove is in connexion with the outer tube, so that, when the tap is turned off, there is still communication between the atmospheres in the vessels above and below the stopcock. The liquid flows from the upper to the lower vessel through the central tube and the bore of the stopcock.

W. P. S.

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## Inorganic Chemistry.

**Recovery of Perchlorate Residues from Potassium Estimations.**

A. VÖRTHEIM (*Chem. Weekblad*, 1918, 15, 581—584. Compare A., 1917, ii, 568).—The usual method for the recovery of perchloric acids is to transform all the reagent into its potassium salt, which is easily purified by recrystallisation, and to distil the mixture of this salt with an excess of sulphuric acid in a vacuum. This method allows of recovery of only 25% of the quantity of acid originally used, and, moreover, requires a good vacuum pump. A method has now been devised which consists of the addition of unslaked lime to the collected alcoholic filtrates, filtration and washing of the precipitate with alcohol, and recovery of the mixed perchlorates of calcium, sodium, and magnesium by distilling off the alcohol. The solid residue is warmed in a basin with sufficient 50% sodium carbonate to convert the mixed salts completely into the sodium compound, the whole filtered, and the filtrate concentrated to crystallisation point. A large excess of 40% hydrochloric acid is added, the clear liquid decanted from the precipitated sodium chloride, the last drops being separated on a vacuum filter, and the solution of sodium perchlorate concentrated to D 1.125. A series of determinations carried out with recovered material gave uniformly higher results than duplicate tests carried

out with pure perchloric acid. Investigation showed that the presence of sodium perchlorate in the recovered material diminishes the solubility of the potassium salt, and that therefore more accurate results are obtained by using the recovered material than by working with chemically pure perchloric acid. S. I. L.

**Appearance of Fogs in Chemical Reactions.** VIKTOR ROTHMUND (*Monatsh.*, 1918, **39**, 571—601).—The nature of the fogs produced in certain chemical reactions has been investigated. In the case of the fogs produced when ozone enters into reaction with a large number of reagents (particularly reducing agents), it is shown that the fog consists mainly of water in which a small quantity of the products of the reaction are dissolved. These fogs only occur when the reducing agent is of a volatile nature and when the reaction products are soluble in water. The size of the fog particles is practically the same in a number of very different reactions. The approximate diameter as calculated from the rate of subsidence is  $10^{-4}$  cm. The stability of the liquid drops in saturated water vapour is explained by the increased curvature brought about by the solution of the products of the reaction which effect a reduction of the vapour pressure. In the case of ozone and hydriodic acid, a larger value is calculated for the diameter, and this is explained by the formation of hydrogen peroxide. The ammonium chloride fogs, the fogs from fuming acids, fogs produced by the action of radium emanation on sulphur, carbon disulphide, camphor, and iodine, as well as the electrically produced and atmospheric fogs, are also considered. In all cases, the fog produced shows an analogous behaviour to the ozone fogs and generally has drops of about the same size. J. F. S.

**The Waters of the Atlantic Ocean on the Argentine Coasts.** HERCULES CORTI and HÉCTOR H. ALVÁREZ (*Anal. Soc. Quim. Argentina*, 1918, **6**, 108—120).—A detailed study of samples of sea-water taken under varying conditions at different places on the Argentine coast.

Extensive tabular statements are given of chemical composition and of general and physico-chemical properties. The methods of analysis adopted are briefly indicated. W. S. M.

**Synthesis of Sulphuryl Chloride in Presence of Organic Compounds.** GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1918, [v], 27, ii, 201—204).—The keto-cineole described by the author and Linari (*A.*, 1912, i, 272) is similar in many of its chemical properties to camphor, which it may replace in the preparation of sulphuryl chloride from sulphur dioxide and chlorine by Schulze's method. The reaction,  $\text{SO}_2 + \text{Cl}_2 = \text{SO}_2\text{Cl}_2$ , is also accelerated by cyclohexanone, menthone, or tetrahydrocarvone, but does not occur in presence of  $\alpha$ -bromocamphor, Reyckler's camphorsulphonic acid, camphorquinone, or monobromo- or monochloro-ketocineole (to be described elsewhere) with the halogen attached to the methylene contiguous to the carbonyl group; the reaction is, however,

activated by introducing into the compounds just named a positive radicle, for instance, by transforming the sulphonic acid into either the amide or the anilide, or camphorquinone into the monoxime or isonitrosocamphor. Pernitrosocamphor also catalyses this reaction, but not the anilide of chlorocamphorsulphonic acid. These results are not in disagreement with the view that the catalytic action of camphor is connected with the formation at low temperatures of one or more compounds of sulphur dioxide with camphor.

T. H. P.

**New Method for the Synthesis of Ammonia.** H. HAMPEL and R. STEINAU (*Chem. Zeit.*, 1918, **42**, 594).—Metallic iron, ammonium chloride, and nitrogen are heated together at 300° under 50 atmospheres pressure. The reaction proceeds according to the equation  $3\text{Fe} + 6\text{NH}_4\text{Cl} + 2\text{N} = 3\text{FeCl}_2 + 8\text{NH}_3$ . A gaseous mixture is obtained containing up to 99% of ammonia. The portion of this derived from the ammonium chloride may be allowed to react with the ferrous chloride; the ferrous hydroxide formed is reduced and the ammonium chloride recovered for further use. [See, further, *J. Soc. Chem. Ind.*, 1919, February.] W. P. S.

**Mixtures of Nitrogen Peroxide and Nitric Acid.** WILLIAM ROBERT BOUSFIELD (*T.*, 1919, **115**, 45—55).

**Oxidation Pressure Limits (A Theory of the Pressure Limit in Autoxidation).** W. P. JORISSEN (*Chem. Weekblad*, 1918, **15**, 705—714).—A résumé of the observations and measurements on the lower limit of pressure in the autoxidation of phosphorus in oxygen, and of the theories which have been advanced to account for the facts observed.

The author considers the phenomenon to be a particular case of the ignition of an inflammable gas mixture (phosphorus vapour and oxygen) whenever the ratio of combustible constituent to oxygen becomes sufficiently large, the temperature in this case being sufficiently high to cause spontaneous ignition. W. S. M.

**The Atomic Structure of Carborundum determined by X-Rays.** C. L. BURDICK and E. A. OWEN (*J. Amer. Chem. Soc.*, 1918, **40**, 1749—1759).—The angle between the edges of the elementary rhombohedron of carborundum, which crystallises in the ditrigonal pyramidal class of the hexagonal system, is 89°56'; the departure from the simple cube being due to a shortening by only 0·15% of one trigonal axis of the cube. The results of the X-ray measurements here recorded, using rays from a palladium target, show a very close relationship between the crystal structure of carborundum and that of diamond. The silicon and carbon atoms in the carborundum crystal are each arranged on face-centred rhombohedral (nearly cubic) lattices. In the prism planes (10 $\bar{1}$ 0) and (11 $\bar{2}$ 0), the carbon and silicon atoms lie in the same planes, from which it follows that in the direction of the principal

axis the carbon and silicon atoms alternate, there being no lateral displacement between the two kinds of atom with respect to this axis. From the relative intensities of the reflections of the spectra of different orders by the different planes, the displacement of the carbon planes from the silicon planes in the direction of the principal axis is calculated to be equal to 0.36 of the distance between two consecutive carbon or silicon planes. The carborundum structure can then be derived from that of the diamond by replacing the carbon atoms of one of the two interpenetrating face-centred cubic lattices of the diamond by a similar lattice of silicon atoms, shortening one trigonal axis by 0.15%, and displacing the atoms of one lattice from a position 0.25 to one 0.36 of the distance between successive planes of the other lattice in the direction of the shortened axis.

From the values of the distances between the atom planes derived from the measurements, the density of carborundum is calculated to be 3.11, the observed value being 3.123. E. H. R.

**Electrolysis of Potassium Phosphate.** A. RIUS Y MIRÓ (*Anal. Fis. Quim.*, 1918, **16**, 573—610).—The electrolytic oxidation of potassium phosphates is assumed to take place in two stages, the first being the formation of perphosphate and the second that of monoperphosphate. For dipotassium hydrogen phosphate, the primary reaction can be represented by the equation  $2K_2HPO_4 + O = K_4P_2O_8 + H_2O$ . The perphosphate then undergoes further oxidation to monoperphosphate,  $K_4P_2O_8 + O + H_2O = 2K_2HPO_5$ .

A. J. W.

**The Fusion of Sodium Hydroxide with some Inorganic Salts.** MAITLAND C. BOSWELL and J. V. DICKSON (*J. Amer. Chem. Soc.*, 1918, **40**, 1773—1779).—When certain salts which can function as oxygen acceptors are fused at high temperatures (300—400°) with sodium hydroxide, the salt is oxidised and hydrogen evolved. Quantitative experiments have been made with sodium arsenite and ferrous sulphate, and it is found that the hydrogen given off is equivalent to the oxygen taken up by the salt. Stannous chloride and vanadium sulphate are also oxidised, and cerous and uranous sulphates to a small extent. It is remarkable that such readily oxidisable salts as sodium nitrite and sodium sulphite are not oxidised when fused with sodium hydroxide. It is perhaps noteworthy that all the bases the salts of which were found to be oxidised belong, with the exception of iron, to groups 4, 5, or 6 of the periodic table.

The mechanism of the reaction consists ultimately in the decomposition of water, the oxygen carrying the oxygen acceptor to a higher stage of oxidation, whilst the hydrogen is evolved as gas. The general oxidising action of water catalysed by sodium hydroxide is also shown by the evolution of hydrogen when such metals as zinc and aluminium are boiled with sodium hydroxide solution.

E. H. R.

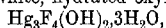
**Some Properties of Magnesium Ammonium Phosphate and Magnesium Pyrophosphate.** Z. KARAOGLANOV and P. DIMITROV (*Zeitsch. anal. Chem.*, 1918, **57**, 353—371).—The conversion of magnesium ammonium phosphate into magnesium pyrophosphate by ignition sometimes is and sometimes is not accompanied by incandescence. The presence or absence of the phenomenon is found to depend on the conditions under which the magnesium ammonium phosphate is precipitated. If precipitated slowly at the boiling temperature, the product does not incandesce, but if formed quickly at lower temperatures, it invariably does, whether precipitated from a magnesium solution or from a phosphoric acid solution. The pyrophosphate formed with incandescence is grey to black in colour, whilst that formed without incandescence is quite white. The authors conclude from their experiments that only samples of magnesium ammonium phosphate which contain traces of organic matter will incandesce on ignition, since when organic matter, such as filter paper, is carefully excluded, no incandescence is observed. There are apparently two modifications of magnesium pyrophosphate, differing considerably in physical properties. The one, formed without incandescence, is loose in texture and white in colour; the other, the formation of which is always accompanied by incandescence, is hard and lava-like, grey to black in colour, and more resistant to hydrochloric and nitric acids. Its colour is due to enclosed particles of carbon, and is only with difficulty removed at a very high temperature by ignition, but can be destroyed by treatment with acids or an oxidising agent, such as ammonium nitrate. The incandescence of any sample of magnesium ammonium phosphate can be prevented by evaporating it before ignition with an ammonium salt or by heating very slowly to the decomposition temperature. The opinion of Balareff (A., 1917, ii, 90) that the properties of the magnesium pyrophosphate obtained depend on the vapour tension (degree of hydration) of the magnesium ammonium phosphate before calcination is shown to be incorrect. E. H. R.

**Adsorption of Metals from Drinking Water by Glass.** K. SCHERINGA (*Pharm. Weekblad*, 1919, **56**, 8—9).—The proportion of lead in drinking-water can considerably diminish within a few hours. It is known that if an aqueous magenta solution be boiled in a glass vessel, the latter cannot afterwards be cleaned in the ordinary way; this absorption, however, does not occur if the vessel has been previously cleaned carefully with soap and water and afterwards well rinsed out. Since, then, organic dyes are not adsorbed by a cleaned glass surface, it appears very doubtful that metallic salts should be so adsorbed. This conclusion was confirmed by estimating colorimetrically solutions of various salts which had been allowed to remain for two days in carefully cleaned glass vessels. In no case was the slightest diminution of the amount of metal in solution detected. It appears, therefore, that the diminution in the case of lead is due to chemical action, either

by disturbance of an equilibrium when the water is removed from contact with the lead, or by precipitation of finely divided lead carbonate.

S. I. L.

**Anhydrous Mercuric Fluoride.** OTTO RUFF and GUSTAV BAHLAU (*Ber.*, 1918, 51, 1752—1760).—*Anhydrous mercuric fluoride* may be prepared by heating mercurous fluoride in a current of dry chlorine at 275°, or of dry bromine at 400°, or by heating mercurous fluoride at 450° under 10 mm. pressure. Mercuric fluoride forms transparent, octahedral crystals, m. p. 645°; its b. p. is estimated at 650°. It has  $D^{25}_4$  8.95. Attempts to determine the vapour tension at various temperatures did not yield satisfactory results, since the vessels are attacked by the vapours. The substance is very sensitive to moisture and becomes discoloured by traces of water vapour, which are not analytically demonstrable; on exposure to air, hydrogen fluoride is evolved, and mercuric oxyfluoride and, ultimately, mercuric oxide, remain. With small quantities of water, a white, hydrated oxyfluoride,



is formed, whilst with larger quantities, mercuric oxide is gradually produced. Mercuric fluoride dissolves in hydrofluoric acid solution (40%), and, on cautious evaporation, the hydrated fluoride,  $\text{HgF}_2 \cdot 2\text{H}_2\text{O}$ , is obtained in small, colourless crystals. The vapours of mercuric fluoride attack platinum above 500°; mixtures of the fluoride with silver, copper, lead, aluminium, magnesium, zinc, tin, chromium, iron, or arsenic react vigorously when strongly heated locally, yielding amalgams and metallic fluorides, the latter being easily isolable in the pure condition if an excess of mercuric fluoride is used. Sulphur tetrafluoride appears to be formed when mercuric fluoride is heated with sulphur, but no reaction occurs with amorphous or graphitic carbon. The fluorine does not appear to be replaced when the fluoride is heated in a stream of chlorine or bromine.

*Mercuric chlorofluoride*,  $\text{HgClF}$ , is obtained as a pale yellow substance by passing dry chlorine over mercurous fluoride at 120°; the pale yellow *bromofluoride* is similarly prepared at 105°.

The preparation of mercuric fluoride in quantity is best effected by the process first described.

H. W.

**Double Catalytic Process in the Oxidation of Aluminium in the Presence of Mercury. Oxidation of Aluminium Powder at the Ordinary Temperature.** P. RONCERAY (*Bull. Sci. Pharmacol.*, 1918, 25, 193—198; from *Chem. Zentr.*, 1918, ii, 699).—Aluminium in a fine state of division is oxidised by the air and under water. Pieces of aluminium in contact with iron do not oxidise in water, but in the presence of a small quantity of mercury, aluminium undergoes oxidation through the operation of two catalytic processes. The mercury, owing to the formation of an amalgam, reduces the aluminium to a molecular state, and the mercury oxide produced acts as an agent for the transfer of



oxygen from the air to the aluminium. Pieces of aluminium after rubbing with mercury oxide are rapidly oxidised in the air and under water.

H. W. B.

**Solubility of Aluminium Hydroxide.** E. H. ARCHIBALD and Y. HABASIAN (*Trans. Roy. Soc. Canada*, 1917—1918, [iii], 11, 1—6).—The solubility of aluminium hydroxide in ammonia solutions of different concentrations and in similar solutions to which various amounts of ammonium or potassium nitrate had been added, has been determined at 20° and 30°. The method consisted in shaking the freshly precipitated hydroxide in sealed tubes with the solvent for twelve hours in a thermostat, filtering, evaporating measured weights of the solution in a platinum crucible, igniting, and weighing. The following weights of  $\text{Al}(\text{OH})_3$  dissolve in 100 c.c. of solution of ammonia at 20°:

Normality of  $\text{NH}_4\text{OH}$ , 0.050, 0.100, 0.125, 0.200, 0.500, 1.00.  
Grams of  $\text{Al}(\text{OH})_3$ , 0.0070, 0.0080, 0.0250, 0.0380, 0.0450, 0.0240.

The solubility increases, therefore, with the ammonia concentration to a maximum which lies at 0.5*N*-ammonia, and then decreases. In these experiments, it is shown that the amount of aluminium hydroxide in solution after thirty minutes' shaking is considerably more than the above quantity, but decreases as the shaking proceeds until equilibrium is reached, which is always achieved in less than twelve hours. The presence of ammonium nitrate decreases the solubility of aluminium hydroxide in ammonia, and the decrease is greater the higher the temperature and the concentration of ammonium nitrate. The addition of potassium nitrate increases the solubility of aluminium hydroxide to a very marked extent. It is pointed out that in the quantitative estimation of aluminium, only a small excess of ammonia should be used, and a 10% solution of ammonium nitrate should be used in the washing.

J. F. S.

**Relation between Molecular Structure and the Activity towards Hydrogen Sulphide of Oxide of Iron.** G. WEYMAN (*J. Soc. Chem. Ind.*, 1918, 37, 333—336r).—Iron oxides obtained by heating at 100° to 650° are equally active as regards absorption of hydrogen sulphide in the cold, but at 750° a change occurs, which may also be effected at lower temperatures by very prolonged heating. It seems that the activity of the oxide is dependent primarily of molecular structure, and not on any particular degree of hydration, but the oxide is derived in almost all cases from some form of hydrate.

W. P. S.

**Chromatocobaltiammines.** SAMUEL HENRY CLIFFORD BRIGGS (*T.*, 1919, 115, 67—76).

**The Evolution and Oxidation of Chromic Hydroxide in Alkaline Solution.** F. BOURION and A. SÉNÉCHAL (*Compt. rend.*, 1919, 168, 59—62).—An alkaline solution of chromic hydroxide

undergoes a change on keeping, which tends to make it lose its chemical activity, particularly in respect to its powers of reducing hydrogen peroxide. This change is the more rapid as the concentration of the chromium is greater and of the alkali is smaller. It is, however, possible to oxidise 97% of the chromium in chrome alum to chromate by adding sodium hydroxide to the solution of the alum containing four times the calculated quantity of hydrogen peroxide, and then immediately destroying the excess of peroxide by shaking the solution with manganese dioxide. W. G.

**The Crystalline Structure of Grey Tin.** A. J. BIJL and N. H. KOLKMEIJER (*Chem. Weekblad*, 1918, 15, 1264).—A preliminary note on the crystalline structure of grey tin. The authors have shown that the crystals belong to the regular system.

W. S. M.

**Bismuth Hydride and Polonium Hydride.** FRITZ PANETH (*Ber.*, 1918, 51, 1704—1728).—By application of the methods used in the study of radioactive substances, the author has succeeded in demonstrating that bismuth forms a gaseous hydride which possesses considerable stability at the ordinary temperature and is not decomposed with much greater readiness than antimony hydride; with increasing temperature, the substance rapidly becomes less stable, and is decomposed into its elements at a red heat. The gas can be almost completely condensed by the use of liquid air, and subsequently, in part, regasified.

Bismuth hydride is obtained by the solution of an alloy of magnesium with thorium-*C* or radium-*C* in 0.2*N*-hydrochloric or sulphuric acid. The alloy is prepared by exposing magnesium foil to the radiations of a radiothorium preparation contained in a glass capsule covered with silk paper, which is impermeable to thorium-*X*; shortly after its removal, in consequence of the rapid decay of thorium emanation and thorium-*A*, the deposit consists entirely of thorium-*B* and thorium-*C*. The alloy is placed in a weighing bottle connected with an electroscope in such a manner that a regular current of nitrogen can be sent through the apparatus. After determination of the natural leak of the electroscope, 0.2*N*-hydrochloric acid is dropped on to the alloy; the electroscope soon indicates an activity, which becomes feebler after a few minutes. The results of this and similar experiments show that when magnesium superficially alloyed with bismuth and lead is dissolved in dilute hydrochloric acid, a few thousandths of the bismuth are converted into such a state that they can be carried by a gas current through a cotton wool filter, and that a similar reaction does not occur with lead. A series of control experiments shows that the observed effects are actually due to a volatile compound of bismuth, and not, for example, to the liberation of thorium-*C*, to the selective action of the filter, or to the relatively greater volatility of thorium-*C* chloride.

Polonium hydride is prepared in a similar manner. The alloy

of magnesium and polonium is prepared by the electrolysis of a feebly acid solution of polonium chloride, a piece of magnesium foil being used as cathode. When the alloy is dissolved in dilute acid and the gases evolved are led into an electroscope, an activation is observed which does not decrease in the course of a day, and therefore is caused by polonium. The gas closely resembles bismuth hydride. It is remarkable that a current of oxygen can be used instead of hydrogen or nitrogen for the transport of the gas without sensibly diminishing the yield. The latter is less than in the case of bismuth hydride, and up to the present it has not been found possible to convert more than a few tenths' part per thousand of the polonium into the gaseous state. If the gas current is cooled to  $-84^{\circ}$ , the polonium hydride is only partly condensed. The investigation of the gas is rendered very tedious, since in each experiment the electroscope becomes permanently damaged and does not recover when left to itself for a time.

H. W.

**Bismuth Hydride. II.** FRITZ PANETH and ERICH WINTERNITZ (*Ber.*, 1918, 51, 1728-1743).—The application of radioactive methods having shown that bismuth hydride is capable of existence, and having indicated its mode of preparation and general properties (preceding abstract), the authors now describe attempts to prepare it in weighable quantity from non-radioactive material.

The requisite bismuth-magnesium alloy is prepared by heating equal weights of powdered bismuth and magnesium (as free from silicon as possible) in an iron crucible in a rapid stream of dry hydrogen. The alloy is dissolved in approximately 4*N*-hydrochloric or sulphuric acid (or in some cases nitric acid). Bismuth hydride is thus obtained in sufficient quantity to permit its detection either by the formation of a bismuth mirror or by luminescence tests.

The bismuth mirror is obtained in the usual Marsh's apparatus, and very closely resembles the antimony mirror. As generally obtained, it consists of a strong brown ring in front of and a fainter ring behind the heated spot. The former deposit appears to be frequently burnt into the glass and to be unsuitable for further experiments. This drawback can be overcome by placing a pierced clay disk on the tube and allowing the flame to play against this, as also by increasing the velocity of the gas current. The antimony, arsenic, and bismuth mirrors are most readily distinguished by a number of chemical tests involving the use of sodium hypochlorite, yellow ammonium sulphide, hydrogen sulphide, etc., which are fully described in the original. Attempts to estimate the yield of bismuth hydride by weighing the bismuth mirrors show that about  $5 \times 10^{-3}$  of the bismuth used is converted into the hydride, or that the yield is only about one-twentieth of that obtained from thorium-*C*. It should be noted, however, in this connexion that circumstances have prevented the authors from determining the optimum conditions of experimenting.

The authors have also applied Donau's luminescence method (A.

1913, ii, 743) to the detection of traces of bismuth, and find the procedure very rapid and so sensitive that it is capable of proving the presence of traces of bismuth which cannot be detected by the ring test. For this purpose, the gases issuing from the Marsh's apparatus are ignited, and a piece of pure calcium carbonate is held on a platinum loop in the flame; the bismuth hydride is decomposed, and a portion of the bismuth is deposited on the lime. The latter is allowed to cool, and then placed at the edge of the hydrogen flame, when the presence of bismuth is betrayed by the cornflower-blue luminescence; in similar circumstances, antimony is readily detected by a sky-blue luminescence, both colorations being readily visible in bright daylight.

The absorption of bismuth hydride by various reagents has been examined; the most suitable solution for this purpose appears to be 0.4*N*-silver nitrate solution. Water absorbs the gas to some degree, and 4*N*-sulphuric acid to about the same extent. 0.5*N*-Sodium carbonate solution and *N*-potassium hydroxide solution are more active, whilst the gas is also absorbed by desiccating agents, such as calcium chloride or soda-lime. It is completely decomposed by concentrated sulphuric acid. An aqueous solution of hydrogen sulphide is not more efficient than pure water.

H. W.

**Gold Amalgams.** N. PARRAVANO (*Atti R. Accad. Lincei*, 1918, [v], 27, ii, 168—170; *Gazzetta*, 1918, 48, ii, 123—128).—Objections are raised to the argument of Guertler (*Metallographie*, 524), who concludes that mercury dissolves in gold, giving origin to a solid solution containing at most about 10% of gold, and that in the amalgams containing 90—0% of gold no other crystalline individual is formed. The author has made the following experiments: (1) Definite quantities of saturated amalgam and of gold are placed in a vessel, and the latter exhausted; distillation of the mercury on to the gold then proceeds until the composition of the amalgam formed reaches that of the solid in equilibrium with the liquid amalgam. (2) A current of hydrogen is passed over the amalgam; the quantity of mercury thus transported will be a function of the tension of the mercury of the amalgam provided that, in any series of experiments, the form of the apparatus and the velocity and duration of the gaseous current are maintained constant. The results show that gold amalgams contain at least the two compounds  $\text{Au}_2\text{Hg}_3$  and  $\text{Au}_3\text{Hg}$ .

T. H. P.

**Amalgams. I. Colloidal Gold Amalgam.** C. PAAL and HERMANN STEYER (*Kolloid Zeitsch.*, 1918, 23, 145—158).—Hydrosols of gold amalgam have been prepared (1) by shaking gold sols with metallic mercury, (2) by allowing a gold sol to remain in contact with metallic mercury at rest, (3) by mixing solutions of gold hydrosol with mercury hydrosol, and (4) by precipitating both gold and mercury from a solution of the mixed chlorides in the presence of a protecting colloid. In the last-named case, amalgam hydrosols

of the composition represented by the formulæ  $\text{Au}_3\text{Hg}_2$  and  $\text{Au}_2\text{Hg}$ , were prepared by reducing a mixture of suitable concentration of the two chlorides in alkaline solution by hydrazine in the presence of the sodium salts of protalbic and lysalbic acids. The solutions, after dialysis were evaporated to dryness in a vacuum, and gave brittle substances which possessed a black or greenish-black colour and a metallic lustre. These substances readily dissolved in water with the production of colloidal solutions. The stability, composition, and general properties of the hydrosols varied with the method of preparation.

J. F. S.

**Solubilities of Ammonium Platinichloride, Platinibromide, and Iridichloride and the Separation of Platinum and Iridium.** E. H. ARCHIBALD and JOHN W. KERN (*Trans. Roy. Soc. Canada*, 1917-1918, [iii], 11, 7-16).—The solubility of the ammonium salts of chloroplatinic, bromoplatinic, and chloroiridic acids has been determined at a series of temperatures in water and in solutions of various strengths of ammonium chloride and ammonium bromide. It is shown that 100 grams of water dissolve 0.2902 gram of ammonium platinichloride at  $0^\circ\text{C}$ , 0.365 gram at  $7.2^\circ$ , 0.4869 gram at  $18.0^\circ$ , 0.5760 gram at  $25.4^\circ$ , 0.6370 gram at  $29.9^\circ$ , 0.7870 gram at  $38.9^\circ$ , 1.0131 grams at  $49.7^\circ$ , 1.4740 grams at  $60.2^\circ$ , 1.7440 grams at  $70.0^\circ$ , 2.1800 grams at  $80.2^\circ$ , 2.6150 grams at  $90.0^\circ$ , and 3.2515 grams at  $99^\circ$ . Ammonium platinibromide is somewhat more soluble in water than the foregoing salt; 100 grams of water dissolve 0.4165 gram at  $0^\circ\text{C}$ , 0.5002 gram at  $7.3^\circ$ , 0.6438 gram at  $19.0^\circ$ , 0.7384 gram at  $25.0^\circ$ , 0.8147 gram at  $29.7^\circ$ , 1.0355 grams at  $40.0^\circ$ , 1.2087 grams at  $50^\circ$ , 1.5780 grams at  $60.0^\circ$ , 1.9265 grams at  $70.0^\circ$ , 2.3002 grams at  $80.0^\circ$ , 2.8370 grams at  $90^\circ$ , and 3.5866 grams at  $99^\circ$ . Ammonium iridichloride is much more soluble than either of the platinum compounds; 100 grams of water dissolve 0.5661 gram at  $0.2^\circ$ , 0.7055 gram at  $10.0^\circ$ , 1.0910 grams at  $25.0^\circ$ , 1.2066 grams at  $30.0^\circ$ , 1.5665 grams at  $40.0^\circ$ , 1.9664 grams at  $50.0^\circ$ , 2.4567 grams at  $60.0^\circ$ , and 4.3815 grams at  $80.0^\circ$ . In the presence of ammonium chloride, the solubility of the ammonium salts of chloroplatinic acid and chloroiridic acid is much reduced, but that of the iridichloride is several times as large as that of the platinichloride. Ammonium bromide reduces the solubility of the platinibromide. In all three cases, the reduction in the solubility is proportional to the concentration of the ammonium haloid. The difference in the solubility of ammonium platinichloride and iridichloride furnishes a good method for the complete separation of platinum and iridium. Ammonium platinichloride is appreciably less soluble than potassium platinichloride.

J. F. S.

**Dehydrogenation of Palladium Hydrogen Hydrosol by Metallic and Colloidal Mercury.** C. PAAL and HERMAN STEYER (*Ber.*, 1918, 51, 1743-1752).—It has been previously shown (Paal and Hartmann, A., 1918, ii, 303) that palladium

hydrosol gradually loses its catalytic activity in the presence of metallic or colloidal mercury; in the course of experiments on the action of the hydrosol on mixtures of hydrogen and oxygen in the presence of mercury, it was observed that the catalyst speedily became passive and that the gradual slight absorption of hydrogen was preceded by a temporary increase in the volume of the latter. This phenomenon forms the subject of the present communication, in which it is demonstrated that the palladium hydrogen hydrosol is decomposed by mercury with evolution of hydrogen, and that dehydrogenation is effected more rapidly by metallic than by colloidal mercury. Analysis of the residual palladium hydrosol and of the mercury proves that a portion of the palladium has passed into the mercury, and that some of the latter has passed into the hydrosol. The action of colloidal mercury on palladium hydrogen hydrosol only leads to uniform results when care is taken that only the least possible excess of hydrazine is used as reducing agent in the formation of the mercury hydrosol.

H. W.

### Mineralogical Chemistry.

#### Mineralogy of the H.B. Mine, Salmo, British Columbia.

T. L. WALKER (*Toronto Univ. Studies, Geol. Ser.*, No. 10, 1918, reprint, 25 pp.).—The oxidised zinc-lead ores of this mine consist of a mixture of hemimorphite, cerussite, and limonite, and occur as bedded "veins" in metamorphosed limestone, with associated quartzite and schists, and penetrated by dykes of minette. A cave in the mine contains also a number of zinc phosphate minerals forming large stalactitic pillars, which yielded about a hundred tons of ore. These stalactites consist mainly of a core of spencerite with a thin crust of hemimorphite, and between the two, solution cavities containing crystals of hemimorphite (anal. I, deducting 6.66% calcite), spencerite, hopeite, parahopeite (anal. II, D 3.236), and hibbenite. Crystallographic descriptions are given of each of these minerals, except the hibbenite, the existence of which is not confirmed. On the floor of the cave, and partly coating the stalactites, is a deposit of a grey or cream-coloured, non-plastic, zinciferous clay (anal. III), resembling the so-called moresnetite and vanuxemite in composition, but doubtless a mixture of some zinc mineral with clay. The phosphoric acid of these minerals was perhaps derived from the solution of apatite in the surrounding rocks.

	ZnO.	MgO.	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	SiO <sub>2</sub> .	P <sub>2</sub> O <sub>5</sub> .	H <sub>2</sub> O.	Total.
I. ....	67.35	—	—	—	25.32	—	7.33	100.00
II. ....	54.69	—	—	—	30.46	15.31	100.46	
III. ....	19.90	3.97	16.07	8.01	39.49	0.26	11.12	98.91

The zinc phosphate minerals now known are the following; they

are all remarkable for their chemical purity, there being a complete absence of elements not shown in the formulae:

Hopeite.....	$\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ , orthorhombic	} (A., 1908, ii, 397).
Parahopeite .....	$\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ , triclinic	
Tarbuttite .....	$\text{Zn}_3(\text{PO}_4)_2 \cdot \text{Zn}(\text{OH})_2$ , triclinic	
Spencerite .....	$\text{Zn}_3(\text{PO}_4)_2 \cdot \text{Zn}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ , monoclinic	
Hibbenite.....	$2\text{Zn}_3(\text{PO}_4)_2 \cdot \text{Zn}(\text{OH})_2 \cdot 6\frac{1}{2}\text{H}_2\text{O}$ , orthorhombic	(A., 1916, ii, 629).
	ii, 569).	

L. J. S.

**Examination of the Hot Springs at Banff, Alberta.**  
R. T. ELWORTHY (*Trans. Roy. Soc. Canada*, 1917-1918, [iii], 11, 27-33).—An analysis of the water of, and the gases evolved from, the six hot springs at Banff, Alberta, has been carried out. The upper hot spring contains the following amounts of dissolved solids in parts per million of water: 634,  $\text{SO}_4$ ; 10, Cl; 133,  $\text{HCO}_3$ ; 239, Ca; 39.7, Mg; 9.1, alkalis; 31,  $\text{SiO}_2$ . The total solids amount to 1100 parts per million. Among other metals present are iron, aluminium, manganese, strontium, magnesium, lithium, potassium, and sodium. The gases evolved by the springs contained methane, hydrogen, oxygen, carbon dioxide, nitrogen, helium, and argon. Full analyses are recorded in the paper. These springs are the most radioactive of any yet examined in Canada, the emanation content of the gas being  $(1910-2370) \times 10^{-12}$  curies per litre, whilst that of the water is  $(221-640) \times 10^{-12}$  curies per litre. The dissolved radium is  $(8.5-23.5) \times 10^{-12}$  grams per litre. J. F. S.

**The Thermal Mineral Springs of Rio Hondo.** HÉROULES CORTI (*Anal. Soc. Quím. Argentina*, 1918, 6, 215-229).—A detailed account of the medicinal properties and chemical composition of the thermal springs of Río Hondo, in the province of Santiago del Estero in the Argentine. W. S. M.

### Analytical Chemistry.

**Rational Approximated Atomic Weights for Use in Chemical Analysis.** N. SCHOORL (*Chem. Weekblad*, 1918, 15, 547-562; *Zeitsch. anal. Chem.*, 1918, 57, 209-225).—In ordinary analytical work, it is customary to use for the atomic weights values given to the nearest decimal figure corresponding with the degree of accuracy possible for each determination. In 1904, Erdmann proposed to use atomic weights calculated from hydrogen as unity, since most of the values were very close to whole numbers. Since, however, the atomic weights of one or two of the commonest elements cannot be rounded off to whole numbers without introduction of considerable error, the proposal has found little favour.

The author puts forward the consideration that much more satisfactory values are obtained for analytical purposes by taking account of the fact that, whereas in all accurate atomic weight determinations the weighings are reduced to the proper values for weighing in a vacuum, in analytical work the correction for the weight of air displaced is seldom made. He proposes to use a set of "air atomic weights" obtained from the accepted atomic weights by introducing values based on the air correction. The accepted atomic weight of iodine is, for example, 126.92. Allowing for the difference in specific gravity of iodine and the brass weights generally used in chemical analysis, the volume atom of iodine, namely, 126.92 grams weighed in a vacuum, would weigh in air 126.906 grams. Though the value of this air correction is so small as generally to affect only the third decimal place, it becomes much greater in the cases of carbon, hydrogen, and oxygen, the elements chiefly concerned in organic analysis. The atomic weight of hydrogen is given by the International Committee for 1916 as 1.008. Assuming the atomic volume of hydrogen in combination to be 6, the "air atomic weight" becomes 1.0005, which can without any inaccuracy be given as 1.00 for ordinary purposes. The correction for oxygen, assuming an atomic volume of 6, does not alter the accepted value 16.00, whilst carbon with the accepted atomic weight of 12.005 becomes 11.999, that is, for ordinary purposes 12.00. Similarly, the "air molecular weight" of water becomes 18.00 instead of 18.02 on the basis of the true atomic weights.

The values given in the International table of atomic weights for 1916 have been modified to give the air atomic weights for analytical purposes on the basis of the atomic volumes of the elements. The author devotes many pages to a selection of suitable atomic volumes for each element, basing his calculations on Kopp's law that the atomic volumes are additive. In the case of most of the elements, the values adopted for the atomic volumes are averages of very different figures; the values for cobalt, for example, deduced from the oxide, chloride, bromide, sulphide, and sulphate, respectively, are 7, 9, 2, 1, and 4, the average value, 5, being adopted. As the basis for the calculations for obtaining the atomic volumes of the elements from the specific gravities of their compounds, the following atomic volumes are assumed: O=6, S=16, Cl=15, Br=22, I=31. The atomic volumes of the halogens and of the alkali and alkaline earth metals are taken as approximately half of the values deduced from the atomic weights and the specific gravities.

In order to obtain trustworthy figures for molecular and equivalent weights for ordinary analysis, it is suggested that use may be made of the true molecular volumes of the commoner reagents. The molecular weight of oxalic acid, for example, is 126.058, calculated from the accepted atomic weights. The specific gravity being 1.64, the value to be subtracted to arrive at the "air molecular weight" is 0.076, giving the value for use in volumetric analysis as 125.982. By addition of the air atomic weights given in the



table, the value 125.976 is obtained, which agrees with the figure of 125.982 obtained from the molecular volume better than does the figure 126.058 obtained by addition of the accepted atomic weights. This argument is repeated for the various reagents used in iodine determinations. It is shown, also, that in analysis of organic compounds for the elements, use of the "air atomic weights" would reduce the hydrogen content by nearly 1% of its value, and since in analysis the hydrogen content as a rule is somewhat too high, it is contended that the use of the "air atomic weights" will give more accurate results. S. I. L.

**The Importance of Electrical Conductivity in Analytical Chemistry.**

I. M. KOLTHOFF (*Chem. Weekblad*, 1918, 15, 889—896).—The determination of conductivity can be employed in a great number of cases as an aid in quantitative analysis, and is very simple and easily carried out. The author has indicated a few cases of the application, leaving to later papers the detailed account and the theoretical discussion. The general cases that arise in volumetric work can be divided into two classes: (1) reactions in which all the ions remain in solution; in this case, the conductivity will generally increase; (2) reactions in which ions disappear. In the second class, the conductivity may (a) diminish, (b) remain unaltered, (c) increase. Suppose a material *CD* to be added in solution to a solution of *AB*, and suppose *AD* to be precipitated as a result of the reaction; the nett result is that in the original solution the *B* ions remain, whilst the *A* ions are replaced by *C*. If the specific conductivity of *A* is greater than that of *C*, the conductivity will rise; this occurs, for example, in the neutralisation of a strong acid by a base, the *H* ion being replaced by the ion of the metal of the base. In the titration of hydrochloric acid by means of sodium hydroxide, for example, the conductivity falls rapidly until all the acid is neutralised; if more alkali be added, the conductivity begins sharply to increase. By plotting the conductivity of the solution against the quantity of alkali is added, the conductivity begins sharply to increase. By neutral point of minimum conductivity The application would be of great use, for example, with a strongly coloured solution for which no colour indicator could be used.

If, in the above cases, the conductivity of *A* is equal to that of *C*, which may happen when a precipitate is formed, the conductivity will change very little until the reaction is complete, after which further addition of the second solution causes a rapid increase. Here, also, the measurement can be of importance for analysis, especially where the precipitate forms slowly or is microcrystalline. In the case of neutralisation of weak acids or bases, the conductivity generally increases during the titration, since the slightly dissociated acid is replaced by a highly dissociated salt. Further addition of the base causes a sharp rise in the conductivity, by reason of the presence of the hydroxyl ion. If the values are plotted, the neutral point can easily be determined, and the method

is of wide application in this case, since colour indicators are not available with weak acids and bases.

Further applications are, for example, titration of a weak acid in the presence of a strong acid, determination of the combined alkali in a salt of a weak acid, determination of basic or acidic properties of a substance, as, for example, the acid character of hydrogen peroxide, etc. Similarly, the concentration of an electrolyte can be determined from the conductivity with the help of tables, and determinations of conductivity combined with specific gravities or other physical constants can be used for analysis of a mixture of two electrolytes. In food analysis, also, the determination may be of great use.

S. I. L.

**The Effect of Dilution in Electro-titrimetric Analyses.**  
GILBERT ARTHUR FREAK (T., 1919, 115, 55—61).

**The Quinone Phenolate Theory of Indicators. Spectrophotometric Study of the End Points and Fading of Phenolsulphophthalein Indicators.** CHARLES L. BRIGHTMAN, J. J. HOPFIELD, M. R. MEACHAM, and S. F. ACREE (*J. Amer. Chem. Soc.*, 1918, 40, 1940—1944).—The present communication deals with phenolsulphophthalein and its tetrabromo- and tetranitro-derivatives. It is found that these indicators have a number of properties which make them the best series yet developed. They are twice as deeply coloured as phenolphthalein in alkaline solution and show sharper colour changes. The excess of alkali necessary to produce the end-point of the neutralisation of the indicator does not cause any appreciable fading in either short- or long-time periods in the case of phenolsulphophthalein and its tetrabromo-derivative. The colour of phenolsulphophthalein in phosphate buffer solutions does not fade appreciably even in considerable periods of time.

Standardised stock solutions of phenolsulphophthalein can be kept in an ice-box without appreciable change, or even at ordinary temperatures if care is taken to prevent contamination, and will then show the same absorption index when treated with an excess of alkali at different time periods. Different samples of the same lot of solid phenolsulphophthalein will give the same absorption index when treated with an excess of alkali.

An excess of alkali in solutions of tetranitrophenolsulphophthalein causes a fading of the intense red colour to a light yellow, the time of fading depending on the amount of alkali and other experimental conditions.

Details of the experimental methods are promised in a subsequent paper.

H. W.

**The Elimination of the Volume of a Precipitate.** H. D. STEENBERGEN (*Chem. Weekblad*, 1918, 15, 1268—1269).—It is sometimes convenient, in order to avoid the washing of a precipitate, to make the estimation of a soluble constituent of a solu-

tion in presence of the precipitate. This may be done by diluting the mixture to two known volumes and estimating the concentration of the solution in each case. A simple formula involving the concentrations thus found is given for the correction required for the volume occupied by the precipitate.

W. S. M.

**The Significance of the Electrical Conductivity in the Analysis of Potable Water.** I. M. KOLTHOFF (*Chem. Weekblad*, 1918, 15, 1160—1183).—The determination of the electrical conductivity has been used by Reichert, Kohlrausch and Holborn, and others as a rapid method for estimating the total solid constituents in ordinary potable waters. For this purpose, a mean equivalent weight and a mean equivalent conductivity are assumed. The author shows how untrustworthy are the results obtained by this method with different types of water. A series of measurements on the conductivity of dilute aqueous solutions of those salts which are ordinarily present in drinking-water, such as sodium hydrogen carbonate, chloride and sulphate, potassium nitrate, calcium chloride and sulphate, magnesium chloride, etc., and of binary mixtures of these, establishes the rule that the degree of dissociation of each salt in the mixed solution is that which corresponds with the total concentration of electrolyte, even in the case where the salts have no common ion. By means of this rule, the author has prepared tables which permit the calculation of the equivalent conductivity of a mixture when the chemical composition of the solution is known. The comparison of the calculated and the measured conductivities of a water affords a check on the chemical analysis.

W. S. M.

**Chlorometry.** OCTAVE LECOMTE (*Bull. Sci. Pharmacol*, 1918, 25, 217—218; from *Chem. Zentr.*, 1918, ii, 762—763).—The author estimates the active chlorine in bleaching powder or in hypochlorites by titrating a known quantity of stannous chloride with *N*/10-potassium permanganate first with and then without the addition of the hypochlorite solution.

H. W. B.

**Detection of Hydrogen Chloride in Chloroform.** D. VORLÄNDER (*Ber. deut. Pharm. Ges.*, 1918, 28, 385—388).—Neutral chloroform when shaken with a very small quantity of dimethylaminoazobenzene gives a yellow-coloured solution; if the chloroform contains a trace of free hydrochloric acid, the yellow coloration changes to violet-red. Carbon dioxide and anhydrous formic and acetic acids, in chloroform solution, do not give a red coloration with dimethylaminoazobenzene. [See, further, *J. Soc. Chem. Ind.*, 1919, 55A.]

W. P. S.

**Volumetric Estimation of the Sulphion.** R. HOWDEN (*Chem. News*, 1918, 117, 383).—A rapid, approximate method for the estimation of soluble sulphates of the alkali metals in solution is based on their decomposition by barium carbonate. The solution is shaken with pure precipitated barium carbonate in

presence of phenolphthalein, and standard hydrochloric acid is then run in until the red colour is discharged. The solution is filtered and the titration completed on the filtrate, using methyl-orange as indicator. The addition of acid before filtration appears to be necessary to complete the decomposition of the soluble sulphate by the barium carbonate. [See also *J. Soc. Chem. Ind.*, 1919, 57A.]  
E. H. R.

**Folin's Direct Nesslerisation Method for the Estimation of Nitrogen.** LOVELL LANGSTROTH (*J. Biol. Chem.*, 1918, **36**, 377—380).—Accurate results are obtained even when impure sulphuric acid is employed for the digestion provided the necessary corrections are made, the latter being ascertained by control blank experiments (compare Folin and Denis, A., 1916, ii, 573).

H. W. B.

**Estimation of Phosphorus by the Nephelometric Method.** EDWARD B. MEIGS (*J. Biol. Chem.*, 1918, **36**, 335—346).—Accurate estimations of phosphorus by means of the strychnine molybdate reagent (compare Kober and Egerer, A., 1915, ii, 794) can only be obtained by adhering strictly to the prescribed procedure.

H. W. B.

**Action of Iodine on Hypophosphorous Acid and Phosphorous Acid. Application to the Estimation of Hypophosphites and Phosphites.** BOYER and BAUZIL (*J. Pharm. Chim.*, 1918, [vii], **18**, 321—334).—In sulphuric acid solution, iodine oxidises hypophosphorous acid to phosphorous acid according to the equation  $\text{H}_2\text{PO}_2 + \text{I}_2 + \text{H}_2\text{O} = \text{H}_3\text{PO}_3 + 2\text{HI}$ . This reaction requires about ten hours for completion. The oxidation proceeds a stage further if the solution is treated with an excess of sodium hydrogen carbonate, the phosphorous acid being then converted into phosphoric acid,  $\text{H}_3\text{PO}_3 + \text{I}_2 + \text{H}_2\text{O} = \text{H}_3\text{PO}_4 + 2\text{HI}$ . In this case, two hours' contact is required, and the mixture must be acidified with acetic acid before the excess of iodine added is titrated. [See, further, *J. Soc. Chem. Ind.*, 1919, February.]

W. P. S.

**A Modified Scheibler Apparatus for the Estimation of Carbon Dioxide.** M. J. VAN'T KRUYT (*Chem. Weekblad*, 1918, **15**, 870—872).—In order to meet the need for a Scheibler apparatus at the Agricultural Testing Station at Maastricht, and in view of the shortage of rubber in Holland, a modification of the original apparatus has been made. The rubber bag and the three-necked bottle in which this is contained between the reaction flask and the gas-measuring apparatus have been removed. The error which would have been caused had the carbon dioxide evolved been allowed to come into contact with the water in the measuring vessel is obviated by using water saturated with carbon dioxide.

In its modified form, the apparatus is found to give more accurate results than in the original form.

S. I. L.

**Estimation of Carbon Dioxide in Carbonates.** DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1918, **36**, 351—354).—The carbonate, either pulverised or in solution, is placed at the bottom of a test-tube, 20 to 25 mm. in diameter, which is placed in a 250 c.c. suction flask containing an excess of  $N/10$ -barium hydroxide solution. A rubber stopper carrying a small dropping funnel is inserted into the flask so that the bottom of the funnel dips into the test-tube. The flask is then exhausted to a pressure of 50 mm. or less, and the outlet closed with a screw clamp. An excess of  $N$ -hydrochloric acid, usually about 5 c.c., is admitted slowly from the funnel. When the rapid evolution of carbon dioxide has ceased, the solutions are both agitated by a rotary motion for three minutes. In the case of most substances, this period is sufficient for the complete transfer of carbon dioxide from the inner tube to the barium hydroxide solution. In the analysis of unashed animal tissues, a longer time is necessary, and in the case of bones, at least two hours should be allowed, the solutions being stirred by rotation occasionally during this period and continuously for three minutes at the end of it.

When the reaction is completed, the vacuum is released, the barium carbonate filtered off, and the filtrate titrated with  $N/10$ -hydrochloric acid, using phenolphthalein as indicator.

The method appears to be applicable to all carbonates, soluble or insoluble, in the absence of acids, such as hydrogen sulphide, which are highly volatile from aqueous solution.

H. W. B.

**A Physico-chemical Method of Estimating Alkali Carbonates in the Presence of Alkali Hydroxides. Application to the Analysis of Flue Gases.** RENÉ DUBREISAY, TRIPIER, and TOQUET (*Compt. rend.*, 1919, **168**, 56—59).—If 50 c.c. of various solutions, having the same alkalinity, but containing varying proportions of sodium hydroxide and sodium carbonate, are mixed with 50 grams of phenol, heated until solution is complete, and then allowed to cool, it is found that the temperature at which the solution first becomes turbid is higher as the proportion of sodium carbonate to sodium hydroxide increases. The authors have plotted curves for solutions having, respectively, a total alkalinity of  $2N$ ,  $N$ ,  $N/2$ , and  $N/4$ , showing the relationship of temperature to sodium carbonate present. By means of these, the amount of sodium carbonate in a given solution containing both carbonate and hydroxide may readily be determined by bringing the total alkalinity up to one of the four strengths given above by addition of sodium hydroxide, then proceeding as described above and reading off the amount of sodium carbonate present from the curve.

For the determination of the amount of carbon dioxide present in flue gases, 1 litre of the gas is bubbled through 71.5 c.c. of

$N/4$ -sodium hydroxide, and then the above estimation is carried out on the resulting liquid, the amount of carbon dioxide present in the flue gases being readily calculated from the amount of sodium carbonate found in the solution.

W. G.

**Estimation of Alkali Hydroxide and Alkali Carbonate in Alkali Hypochlorite Solution.** M. PHILIBERT (*J. Pharm. Chim.*, 1918, [vii], 18, 260—272).—The total alkalinity is found by treating a portion of the sample with a measured excess of  $N/10$ -hydrochloric acid and potassium iodide solution, titrating the liberated iodine with thiosulphate solution, then adding potassium iodide-iodate solution, and again titrating the iodine with thiosulphate solution; the latter titration is a measure of the quantity of the added acid which remains uncombined, and the difference corresponds with the alkalinity of the sample. To estimate the free alkali hydroxide, another portion of the solution is treated with a measured quantity of  $N/10$ -barium hydroxide solution, barium chloride solution is also added, the mixture diluted to a definite volume, filtered, and the alkalinity of the filtrate titrated as described above. The difference between the quantities of free and total alkali gives the amount of alkali carbonate. [See, further, *J. Soc. Chem. Ind.*, 1919, February.]

W. P. S.

**Carnot's Method for the Estimation of Potassium Salts.** CAROLINA ETILE SPEGAZZINI (*Anal. Soc. Quim. Argentina*, 1918, 6, 196—209).—Analyses according to the original prescription of Carnot (this Journal, 1877, ii, 921) gave results in every case much too high. The same method as modified by Grandeau and by Fresenius also gave high results.

It is essential in the preparation of the bismuth chloride solution from the subnitrate to give particular attention to the acidity and temperature of the resulting solution, the optimum acidity being determined by precipitation of a known quantity of potassium from  $N/10$ -solution.

Good results were obtained only with pure dilute solutions of potassium chloride ( $N/10$ — $N/1$ ). Nitrate solutions also gave good results, but with sulphate solutions the results were much too low.

With mixtures of potassium chloride and calcium chloride, magnesium chloride, or sodium chloride, the method is satisfactory only when the potassium salt is in excess.

W. S. M.

**Method for the Estimation of Potassium in Blood.** S. W. CLAUSEN (*J. Biol. Chem.*, 1918, 36, 479—484).—Two c.c. of plasma or 1 c.c. of blood are oxidised by boiling with 5 c.c. of a mixture of sulphuric and nitric acids (1:20) for half an hour. The excess of nitric acid is quickly evaporated, and the residual liquid washed into a beaker, rendered alkaline, and then evaporated to dryness. The residue is taken up in glacial acetic acid and the potassium precipitated by sodium cobaltinitrite. The precipitate is collected and then heated with dilute sodium hydroxide, which

changes all the nitrite groups to sodium and potassium nitrite, whilst the cobalt is precipitated as the insoluble hydroxide. The nitrites are then estimated by acidifying with sulphuric acid and titrating with permanganate at 70°.

The method appears to give accurate results.

H. W. B.

**Gravimetric Analysis. VIII. Separation of Calcium from Magnesium.** L. W. WINKLER (*Zeitsch. angew. Chem.*, 1918, **31**, 214—216).—The following method was found to be the most trustworthy for the separation of calcium and magnesium. The neutral solution, measuring 100 c.c. and containing not more than 0.1 gram of calcium and 0.05 gram of magnesium, is treated with 3 grams of ammonium chloride and 10 c.c. of *N*/1-acetic acid, then boiled, and 20 c.c. of 2.5% ammonium oxalate solution are added slowly. The precipitated calcium oxalate is collected after twenty-four hours, dried at 100°, and weighed. The magnesium in the filtrate is precipitated and weighed as ammonium magnesium phosphate (compare A., 1918, ii, 455).

W. P. S.

**Volumetric Estimation of Barium.** THOS. STEEL (*Analyst*, 1919, **44**, 29).—In the method proposed by Waddell (A., 1918, ii, 407), the use of water saturated with barium chromate is recommended for washing the precipitate of barium chromate. [See further, *J. Soc. Chem. Ind.*, 1919, February.]

W. P. S.

**Estimation of Copper by Means of Potassium Thiocyanate, Potassium Iodide, and Thiosulphate.** I. M. KOLTHOFF (*Chem. Zeit.*, 1918, **42**, 609—610).—The process as described by Bruhns is criticised, and modifications are suggested; trustworthy results are obtained if the copper solution is acidified with sulphuric acid after the potassium iodide has been added. The method may be used for estimating the excess of copper in sugar estimations and for estimating copper in the presence of iron, provided that sodium pyrophosphate is added to inhibit the action of ferric salts. [See, further, *J. Soc. Chem. Ind.*, 1919, February.]

W. P. S.

**Estimation of Copper and Sugar.** G. BRUHNS (*Zeitsch. angew. Chem.*, 1918, **31**, 216).—A reply to Schoorl and Kolthoff's modification of the method described originally by the author (A., 1918, ii, 276).

W. P. S.

**A Very Exact and Rapid Method for the Estimation of Mercury in the Majority of its Compounds.** S. PINA DE RUBIES (*Anal. Fis. Quim.*, 1918, **16**, 661—689).—The method proposed is a combination of the method of Rose-Finkener and that of Eschka, combining the accuracy of the former with the rapidity of the latter. A critical discussion of both methods with the modifications introduced by Cumming and Macleod, and Biewend and Holloway, is given, together with a bibliography of recent literature on the subject since 1914.

The new method as applied to the analysis of mercury minerals

is as follows. The mineral is mixed intimately with fine iron powder, and is carefully heated in a porcelain crucible into which is closely fitted as a cover a small crucible of gold or silver for the condensation of the volatilised mercury. The cooling of the upper crucible is effected by means of a small bladder of indiarubber which, when distended by a steam of cold water, is in close contact with the whole interior surface. After cooling, the inner crucible is washed with alcohol, and the weight of the condensed mercury film determined. The results obtained by this procedure showed a maximum error of 0.07%.

In the case of more volatile compounds of mercury, organic and inorganic, anhydrous potassium carbonate and barium peroxide, either separately or mixed, are substituted for the iron powder.

When the substance to be analysed contains much moisture, for example, a solution, a weighed quantity is evaporated to dryness in the porcelain crucible after the addition of sodium sulphide, and the mercury is determined as before.

The method is applicable without special modification to the analysis of mercury fulminate and fulminate mixtures.

W. S. M.

**Analysis of Aluminium Alloys.** A. TRAVERS (*Chim. et Ind.*, 1918, 1, 708—711).—The alloy is heated with sodium hydroxide solution containing a small quantity of sodium carbonate, and the mixture is filtered. The filtrate contains the zinc and aluminium; the zinc is precipitated as sulphide and estimated acidimetrically after precipitation as ammonium zinc phosphate, whilst the aluminium is estimated by Stock's method. The insoluble portion of the alloy is then dissolved in nitric acid, the solution boiled with the addition of ammonium persulphate, the iron and manganese precipitated with ammonia, the precipitate then dissolved in hydrochloric acid, and the iron titrated with titanium trichloride solution; manganese is estimated in a separate portion of the alloy by the persulphate method. If cobalt and nickel are present, they must be separated as sulphides before the manganese is estimated; cobalt is precipitated by means of  $\beta$ -nitrosonaphthol. The magnesium is estimated in the filtrate from the iron and manganese precipitates, and copper is estimated iodometrically in a separate portion of the sample. [See, further, *J. Soc. Chem. Ind.*, 1919, February.] W. P. S.

**Analysis of Aluminium Alloys and Metallic Aluminium.** J. J. FOX, E. W. SKELTON, and F. R. ENNOS (*J. Soc. Chem. Ind.*, 1918, 37, 328—333).—A detailed description is given of methods suitable for the separation of lead, manganese, silicon, copper, tin, iron, zinc, magnesium, and nickel in aluminium and in aluminium alloys containing a low or high proportion of zinc. W. P. S.

**Estimation of Molybdenum in Ferromolybdenum.** W. HOFFNER and O. BINDER (*Chem. Zeit.*, 1918, 42, 564).—A weighed quantity of about 0.5 gram of the sample is heated with



nitric acid (D 1.2), sulphuric acid is then added, and the heating continued until sulphuric acid fumes are evolved; the solution is diluted to 250 c.c., heated with the addition of a few drops of nitric acid, and the iron precipitated with ammonia. The precipitate is dissolved in sulphuric acid and reprecipitated. The two filtrates, which now contain all the molybdenum, are mixed, treated with 50 c.c. of ammonium sulphide, then acidified with sulphuric acid, and heated. The precipitated molybdenum sulphide is collected and weighed, or it may be converted into molybdic acid by ignition. Traces of impurities may be separated by dissolving the molybdic acid in ammonia. Copper, if present, may be separated as described previously (A., 1918, ii, 372).

W. P. S.

**The Precipitation of Zirconium Phosphate.** GEORGE STEIGER (*J. Washington Acad. Sci.*, 1918, 8, 637—639).—In estimating zirconium in minerals by precipitation as phosphate, the composition of the precipitate approximates more closely to that of normal zirconium phosphate as the acidity of the solution increases. The presence of as much free sulphuric acid as possible is advisable to prevent simultaneous precipitation of iron and titanium phosphates, whilst thorough oxidation with hydrogen peroxide is also necessary to prevent titanium precipitating. At least 3%, and possibly as much as 5%, of free sulphuric acid may be present without interfering with the accuracy of the results. Other phosphates, with the exception of those of the rare earth metals, are readily soluble in the acid solution, and may be separated from the filtrate. [See also *J. Soc. Chem. Ind.*, 1919, February.]

C. A. M.

**Analysis of Commercial "Pure" Benzols.** F. BUTLER JONES (*J. Soc. Chem. Ind.*, 1918, 37, 324—327r).—In a mixture containing benzene, thiophen, toluene, carbon disulphide, and "paraffin," the quantity of carbon disulphide is proportional to the difference between the freezing points of the mixture before and after its removal; similarly, the subsequent removal of the thiophen (by means of basic mercuric sulphate) also results in a difference in the freezing point which is proportional to the amount of substance removed. The residual liquid is a mixture of benzene, toluene, and "paraffin"; the difference between its freezing point and that of pure benzene gives the sum of the amounts of toluene and "paraffin" present; the specific gravity of the liquid in conjunction with the freezing point affords a means of estimating these two constituents. A graph is given for solving the four equations involved.

W. P. S.

**Modification of Webster's Test for Trinitrotoluene in Urine.** F. TUTIN (*Lancet*, 1918, ii, 554; from *Physiol. Abstr.*, 1918, 3, 452).—The urine is extracted with ether, acidified with mineral acid, and again extracted with ether; in the second extract.

an azoxy-compound from trinitrotoluene gives a violet coloration with alcoholic potassium hydroxide. The modifications now proposed are in part minor ones, such as the number of times extraction is performed, but an important change consists in extracting the final ether extract with dilute sodium carbonate solution; this removes substances which mask the characteristic colour of the Webster reaction.

H. W. B.

**Estimation of Small Quantities of Ethyl Ether in Ethyl Alcohol.** H. E. Cox (*Analyst*, 1919, **44**, 26—27).—The method depends on the fact that alcohol of 99% and upwards distills unchanged; any ethyl ether present passes over in the first fractions, and a mixture of constant boiling point is not formed. The amount of ethyl ether may therefore be estimated from the specific gravity before and after distillation, the specific gravity of the alcohol being taken as that obtained after removal of the ethyl ether. [See, further, *J. Soc. Chem. Ind.*, 1919, February.]

W. P. S.

**The Use of Diastatic Reagents. (II) The Detection of Pyramidone and the Differentiation of the Naphthols.**

LUCIANO P. J. PALET (*Anal. Soc. Quim. Argentina*, 1918, **6**, 250—257).—To the solution of pyramidone are added some small pieces of the root of lucerne, which contains oxydases and per-oxydases. A violet-blue colour is produced on the root fibres on keeping. The addition of hydrogen peroxide accelerates the appearance of, but does not intensify, the colour. The further addition of  $\alpha$ -naphthol immediately produces an intense wine-red colour characteristically different from that produced by  $\beta$ -naphthol. This constitutes a delicate test for the presence of small quantities of  $\alpha$ -naphthol in  $\beta$ -naphthol.

W. S. M.

**Assay and Estimation of Nitroso- $\beta$ -naphthol.** PAUL NICOLARDOT and LUCIEN VALLI-DOUAIU (*Bull. Soc. chim.*, 1918, [iv], **23**, 455—459).—For the assay, 2 grams of the material dried at 35° are dissolved in 120 c.c. of acetone in the cold, diluted to 200 c.c. with water, and 100 c.c. of this solution is titrated with a 1.5% solution of iron alum previously standardised against pure nitroso- $\beta$ -naphthol, the end-point being shown by means of ammonium thiocyanate as an external indicator.

For an exact estimation, an excess of iron alum is added to the solution prepared as above, and the precipitate formed is left overnight, collected, washed free from iron salts with water, dried at 70°, and weighed. It contains 90.7% of nitroso- $\beta$ -naphthol.

W. G.

**Volumetric Estimation of Reducing Sugars. A Simplification of Scales's Method for Titrating the Reduced Copper without Removing it from the Residual Copper Solution.** W. BLAIR CLARK (*J. Amer. Chem. Soc.*, 1918, **40**, 1759—1772. Compare A., 1916, ii, 117).—The principle of the

method here described is as follows. The sugar solution to be analysed is boiled under standard conditions with a copper citrate-carbonate solution, and the cuprous oxide dissolved by means of hydrochloric acid. Standard iodine solution is then added to oxidise the cuprous salt, and the excess of iodine titrated by means of sodium thiosulphate. To obtain consistent results, it is necessary to carry out the whole operation under exactly standard conditions. These conditions and the strengths of solutions to be used are indicated for quantities of reducing sugar up to 0.075 gram. It is essential, however, for the worker to standardise his own conditions. The sugar factor of the sodium thiosulphate must be determined on a known sample of reducing sugar, using approximately the same quantity as that to be determined and the same conditions of reduction. The ratio of copper to reducing sugar is approximately constant, the greatest variation occurring with small quantities of sugar.

It was found that sucrose in quantities not exceeding 100 mg. per 10 c.c. and 50% ethyl alcohol do not reduce copper citrate-carbonate solution, but 10% formaldehyde effects a small reduction. [See also *J. Soc. Chem. Ind.*, 1919, February.] E. H. R.

**Source of Error in the Use of Picric Acid in Colorimetric Estimations in Biological Fluids.** ALICE RONDE and MARION SWEENEY (*J. Biol. Chem.*, 1918, **36**, 475—477).—It is shown that picric acid which has been preserved in a moist condition for several months loses some of its power of precipitating chromogenic substances in the blood. The use of such picric acid for the estimation of dextrose in the blood by the Benedict-Lewis colorimetric method would yield too high values. H. W. B.

**The Colorimetric Estimation of Sugar in the Blood by the Reduction of Picric Acid.** C. SALOMON (*Biochem. Zeitsch.*, 1918, **90**, 39—52).—As a result of the critical examination of the method of Lewis and Benedict and its modifications, the author arrives at the conclusion that it has considerable value as regards accuracy and speed for clinical investigations. S. B. S.

**Estimation of Dextrose in the Blood.** F. HAMEL (*Bull. Sci. Pharmacol.*, 1918, **25**, 223—224; from *Chem. Zentr.*, 1918, ii, 769).—Ten c.c. of venous blood are treated with 10 c.c. of a 10% solution of trichloroacetic acid, and, after removal of the precipitated protein, the dextrose is estimated by Fehling's solution in the usual way. H. W. B.

**Estimation of Sugar in Milk and Urine.** B. SJOLLENA (*Chem. Weekblad*, 1918, **15**, 1483—1485).—The method of Folin and Denis (*A.*, 1918, ii, 208) for estimating sugar in milk and urine is recommended. A. J. W.

**Estimation of Lactose.** E. HILDT (*Compt. rend.*, 1918, **167**, 756—759).—For the determination of lactose in milk in which

the sugar has undergone more or less hydrolysis, the author recommends completing the hydrolysis by means of sulphonic acids, such as those of benzene or phenol or those described by Twitchell (A., 1900, ii, 296), and determining the cupric reducing power. One  $\frac{1}{10}$  solution of these acids hydrolyse 0.5% solutions of pure lactose in four hours at 100°, but milk serum requires longer heating. No destruction of galactose occurs as when mineral acids are employed. In the determination of reducing power, using 10 c.c. of boiling alkaline copper solution, 0.0506 gram of hydrolysed lactose is equivalent in reducing power to 0.0708 gram of lactose hydrate or 0.0495 gram of invert-sugar.

Considerable destruction of sugar takes place when the solids of milk which has become unsound are dried at 100°; this is attributed to the formation of melanoidins (see Maillard, A., 1912, i, 169) by interaction of sugar and proteolytic products. [See, further, *J. Soc. Chem. Ind.*, 1919, 51A.] J. H. L.

**Micro-estimation of Lipoids by Titration.** IVAR BANG (*Biochem. Zeitsch.*, 1918, **91**, 86—103).—The fats are oxidised by a 10-potassium chromate solution at the ordinary temperature in presence of excess of sulphuric acid. Excess of chromate solution is then estimated by the addition of potassium iodide and the titration of the liberated iodine by thiosulphate solution. The fat (from blood, etc.) is taken up in benzene solution, a little alkali is added (to emulsify the fat), and then the solvent is distilled off. Cholesterol can be estimated in the same manner (and the same factor is used in making the calculations; this factor is determined empirically, as under the conditions of experiment employed, the oxidation is not complete). When cholesterol is present with fats, the determination of both constituents can be made by precipitation of the cholesterol as digitonide, which is insoluble in benzene. When cholesterol esters are present with fats, the determination of the amounts of the constituents can be made in two ways. Either a strength of alkali can be employed which will hydrolyse the fats, but not the cholesterol ester, which can then be separated from the soaps by benzene, or sufficient alkali can be added to saponify both fats and cholesterol esters, and the cholesterol can then be extracted by benzene and estimated separately. In another portion, fats and esters can be estimated together by oxidation. A series of experiments on the oxidation of the lecithides is also described. S. B. S.

**The Micro-estimation of the Lipoids of the Blood.** IVAR BANG (*Biochem. Zeitsch.*, 1918, **91**, 235—256).—An amplification of the author's micro-method (preceding abstract) is given. Cholesterol and neutral fats are extracted first by a fraction of light petroleum of low boiling point containing chiefly pentane. These can be separated by the method already given, using the digitonin compound of cholesterol. After extraction with petroleum, the blood is extracted with 92% alcohol in the cold. This fraction contains the phosphatide and the cholesterol esters. S. B. S.

**Gravimetric Estimation of Glycyrrhizin.** A. ASTRIC and (Mlle.) G. PICHARD (*J. Pharm. Chim.*, 1918, [vii], 18, 289—290).—Three grams of dry liquorice extract are dissolved in 30 c.c. of water containing five drops of ammonia, the solution is filtered, and 20 c.c. of the filtrate are treated with 2.5 c.c. of sulphuric acid; the precipitated glycyrrhizic acid is collected after twenty-four hours, washed with 30 c.c. of water, then dissolved in ammonia, and the solution evaporated. The residue is dried at 100° and weighed; to the weight obtained is added 0.04 gram as a correction for the solubility of the glycyrrhizic acid in the wash-water. [See, further, *J. Soc. Chem. Ind.*, 1919, February.]

W. P. S.

**A New and Delicate Reaction of Pyramidone and its Differentiation from Antipyrine.** LUCIANO P. J. PALET (*Anal. Soc. Quim. Argentina*, 1918, 6, 151—155).—The author finds that an acid solution of pyramidone when treated with a few drops of an acid solution of potassium ferrieyanide and ferric chloride gives an intense blue coloration and precipitate of Prussian-blue. The test is very delicate. With antipyrine, a blood-red colour is obtained with the same reagent. This colour is converted into a pale yellow by the addition of a few drops of hydrochloric acid. The test is therefore carried out in hydrochloric solution, which permits the blue due to the presence of pyramidone in a mixture to emerge. In this way, 1/100 part of pyramidone may be detected in one part of antipyrine.

Phenacetin, acetanilide, aspirin, exalgin, and caffeine give no reaction with the reagent.

W. S. M.

**The Reaction of the "Ferri-ferric" Reagent with Alkaloids, Glucosides, and other Vegetable Principles.** LUCIANO P. J. PALET (*Anal. Soc. Quim. Argentina*, 1918, 6, 156—158).—An extension of the application of a mixed solution of potassium ferrieyanide and ferric chloride as a reagent (see preceding abstract) to the characterisation of alkaloids, glucosides, and other substances of vegetable origin.

Of 102 substances of this kind tested, 42 gave a positive reaction, that is, a more or less intense blue coloration.

W. S. M.

**Estimation of Phenacetin and other *p*-Aminophenol Derivatives by Means of Hypochlorous Acid.** A. D. POWELL (*Analyst*, 1919, 44, 22—25).—For the estimation of *p*-aminophenol, *p*-phenetidine, etc., the substance is treated with hydrochloric acid and sodium hypochlorite solution, the excess of chlorine is removed by a current of air, potassium iodide is then added, and the liberated iodine titrated with thiosulphate solution. In the first phase of the reaction, *p*-benzoquinonechlorimine is formed; this, after the removal of the excess of chlorine, reacts with hydriodic acid, liberating four atoms of iodine, *p*-aminophenol being re-formed. In the case of phenacetin, a preliminary boiling for two hours with hydrochloric acid is necessary. Each c.c. of *N*/10-thiosulphate

solution is equivalent to 0.00273 gram of *p*-aminophenol, 0.00343 gram of *p*-phenetidine, or 0.00448 gram of phenacetin. [See, further, *J. Soc. Chem. Ind.*, 1919, February.] W. P. S.

**Arsenotungstic and Arsenotungstomolybdic Complexes as Reagents for Phenolic Amines.** LUIS GUGLIAMELLI (*Anal. Soc. Quim. Argentina*, 1918, **6**, 185—195).—Reagents prepared by boiling solutions of sodium tungstate with arsenic acid, and a mixture of sodium tungstate and molybdate with arsenic acid, until concentrated hydrochloric acid no longer produces a precipitate, have been shown to give delicate colour reactions with phenols and some purine derivatives. The same reaction, that is, an intense blue colour, is given by phenolic amines. The author has investigated a large number of substances of this class, and also nitro-sulphonic, and hydroxy-derivatives of these. Positive results were given with the first reagent with the substances  $\text{NH}_2\text{OH}$ ,  $\text{NH}_2\text{NH}_2$ ,  $\text{NHR-NH}_2$ ,  $\text{NHR-NHR}$ ,  $\text{NHR-OH}$ , and also with compounds containing the same groups separated from each other, but united directly to a benzene, naphthalene, purine, or pyrazolone nucleus. The second reagent reacts with substances containing the same groups, and, in addition, with substances containing one amino-group, for example, aniline. W. S. M.

**Estimation of the Carbamide Fraction in Blood.** HEINRICH SCHUR and FRANZ URBAN (*Wien. Klin. Wochenschr.*, 1918, **31**, 892—896; from *Chem. Zentr.*, 1918, ii, 673).—The blood serum is freed from albumin by treatment with sulphosalicic acid solution (20%); nitrogen is estimated by means of bromine and sodium hydroxide in accordance with the method of Knop and Hüfner. H. W.

**Detection of Quinine.** HANS SALOMON (*Ber. deut. pharm. Ges.*, 1918, **28**, 273—275).—The green coloration obtained when a quinine solution is treated with chlorine and then with ammonia will detect 1 part of quinine in 10,000. The fluorescence observed when a quinine solution is treated with dilute sulphuric acid will detect 1 part of the alkaloid in 200,000 parts. It is advantageous to use bromine-water in place of chlorine in the above test, since it is easier to add just the requisite quantity; the bromine is added until the solution is coloured slightly yellow. Another sensitive reagent for quinine consists of potassium iodide (10 grams), mercuric chloride (2.7 grams), water (200 grams), and glacial acetic acid (2.5 grams). [See, further, *J. Soc. Chem. Ind.*, 1919, 54A.] W. P. S.

**Estimation of Quinine in Animal Tissues.** W. RAMSDEN, I. J. LIPKIN, and E. WHITLEY (*Ann. Trop. Med. Parasitol.*, 1918, **12**, 233—258).—See this vol., i, 106.

**Estimation of Morphine in Complex Products. I. Revision of the Analytical Reactions Involved.** ALFRED TINGLE (*Amer. J. Pharm.*, 1918, **90**, 689—706).—A discussion of

various methods and reactions used in the estimation of morphine; the acidimetric method and iodometric method (depending on the formation of the periodide) are trustworthy, but the iodoacidimetric method cannot be used. In methods where the morphine is precipitated by ammonia, the presence of alcohol should be avoided. Barium hydroxide solution does not dissolve morphine completely in the presence of lead acetate. The statement in the British Pharmacopœia that morphine tartrate gives the reactions of morphine and of tartrates is substantially correct. [See further, *J. Soc. Chem. Ind.*, 1919, 27A.] W. P. S.

**Estimation of Morphine in Complex Products. II. Mixtures containing Morphine as a Simple Salt.** ALFRED

TINGLE (*Amer. J. Pharm.*, 1918, 90, 788—795).—The following method is described for the estimation of morphine in powders, pills, etc., provided that the alkaloid is not present in the form of opium. Six grams of the sample are warmed with 2 grams of calcium carbonate and 20 c.c. of water until disintegrated, 60 c.c. of cold saturated barium hydroxide solution are then added, the mixture is shaken, diluted to 100 c.c., and filtered. Fifty c.c. of the filtrate are treated with dilute sulphuric acid in quantity just sufficient to precipitate the barium, the mixture then diluted to 55 c.c., and filtered. Fifty c.c. of this filtrate are neutralised with sodium hydroxide solution, then rendered slightly acid with hydrochloric acid, evaporated to 5 c.c., and extracted five times with a mixture of chloroform and alcohol (2:1) after the solution has been rendered alkaline by the addition of a slight excess of saturated sodium hydrogen carbonate solution; 25 c.c. of the solvent are used each time. The residue obtained on evaporating the solvent from the extract is titrated with *N*/10-sulphuric acid, using cochineal or lacmoid as indicator. [See further, *J. Soc. Chem. Ind.*, 1919, 54A.] W. P. S.

**Estimation of Tyrosine in Proteins.** CARL O. JOHNS and

D. BREESE JONES (*J. Biol. Chem.*, 1918, 36, 319—322).—Tyrosine can be estimated in a protein after hydrolysis with hydrochloric acid by means of the colorimetric method of Folin and Denis (*A.* 1912, ii, 1012). Tryptophan and hydroxytryptophan are destroyed during the hydrolysis, and their decomposition products, as well as oxyproline, do not give any colour with the Folin-Denis reagent.

H. W. B.

**New Contact Test for Albumin in Urine.** U. P. STEWART (*J. Amer. Med. Assoc.*, 1918, 71, 1050; from *Physiol. Abstr.*, 1918, 3, 451).—The reagent is an aqueous solution of picric acid, magnesium sulphate, and citric acid.

H. W. B.

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" " " " (Single Parts)	per part		5	0	7	6
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The specific rotatory power of a specimen of the hydrobromide (containing 2.4 per cent. of water) was determined in aqueous solution:

$\alpha_D + 0.56^\circ$ ;  $c = 3.858$ ;  $l = 2$  dm.;  $[\alpha]_D + 7.4^\circ$  for the anhydrous salt.

*Conessine hydrogen oxalate* forms prisms readily soluble in hot, but rather sparingly so in cold, water, and sparingly soluble in alcohol. It melts and decomposes at  $280^\circ$  (corr.), and is anhydrous.

Found: C=62.5; H=8.1.

$C_{24}H_{40}N_2 \cdot 2C_2H_2O_4$  (536.5) requires C=62.6; H=8.3 per cent.

### *Holarrhenine*, $C_{24}H_{38}ON_2$ .

The crude base was first purified by crystallisation from ethyl acetate, when it melted at  $190^\circ$ , and then converted into the hydrobromide. This salt was crystallised from water and washed with acetone. It was then reconverted into the base, and this was recrystallised from ethyl acetate, when it separated in silky needles which melted at  $197-198^\circ$  (corr.). It suffers no loss at  $100^\circ$ . It is insoluble in water, readily soluble in alcohol or chloroform, but sparingly so in cold ethyl acetate, acetone, or ether.

Found: C=77.5, 77.6, 77.3; H=10.2, 10.3, 10.7; N=7.7; Me(attached to N)=11.1, 12.2.

$C_{24}H_{38}ON_2$  (370.4) requires C=77.8; H=10.3; N=7.6;

Me(attached to N)=12.2 per cent.

The specific rotatory power was determined in chloroform solution:

$\alpha_D - 0.75^\circ$ ;  $c = 5.248$ ;  $l = 2$  dm.;  $[\alpha]_D - 7.1^\circ$ .

The *hydrobromide* crystallises from water in flat needles, which melt at  $265-268^\circ$  (corr.) after drying. It is readily soluble in hot, somewhat sparingly so in cold, water. The air-dried salt contains  $3H_2O$  (Found:  $H_2O = 9.0$ . Calc.:  $H_2O = 9.2$  per cent.).

Found, in salt dried at  $100^\circ$ , C=54.4; H=8.2; Br=29.8.

$C_{24}H_{38}ON_2 \cdot 2HBr$  (532.3) requires C=54.1; H=7.6; Br=30.0 per cent.

The specific rotatory power was determined in aqueous solution:

$\alpha_D + 1.02^\circ$ ;  $c = 4.630$ ;  $l = 2$  dm.;  $[\alpha]_D + 11.0^\circ$  or  $+12.1^\circ$  for the anhydrous salt.

*Acetylholarrhenine*, prepared by the action of acetic anhydride and anhydrous sodium acetate on holarrhenine, crystallises from acetone in large, colourless, oblong plates which melt at  $180^\circ$  (corr.).

It is insoluble in water, sparingly soluble in cold alcohol, acetone, or ether, but readily so in chloroform.

Found : C=75.7; H=9.9; N=6.8.

Equivalent to HCl, using methyl-orange=202.

$C_{26}H_{40}O_2N_2$  (412.5) requires C=75.7; H=9.8; N=6.8 per cent.

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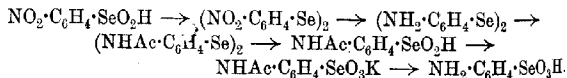
DARTFORD, KENT,

[Received, February 4th, 1919.]

### XIX.—*Meta*-substituted Aromatic Selenium Compounds.

By FRANK LEE PYMAN.

At the suggestion of Dr. Charles Walker, of Glasgow, attempts were made, in 1913, to form the selenium analogue of arsanilic acid, namely, *p*-aminophenylselenic acid,  $NH_2 \cdot C_6H_4 \cdot SeO_3H$ , in order to determine its physiological action. Whilst aniline sulphate and arsenate readily yield sulphanilic acid and arsanilic acid, respectively, at an elevated temperature, no similar compound could be obtained from aniline selenate. It was found, however, that phenylselenious acid gave on nitration a *nitrophenylselenious acid*, which is shown to be the meta-compound in the manner described below. On reducing this compound with sodium hydrogen sulphite, *di-m-nitrophenyl diselenide* resulted, and gave *di-m-aminophenyl diselenide* on further reduction with sodium sulphide. *Di-m-aminophenyl diselenide* gave on acetylation *di-m-acetylaminophenyl diselenide*, from which *m-acetylaminophenylselenious acid* was obtained by oxidation with nitric acid. From this, the salts of *m-acetylaminophenylselenic acid* were obtained on oxidation with potassium permanganate, whilst on attempting to liberate the free acid, hydrolysis took place with the formation of *m-aminophenylselenic acid*:



When these results were first communicated to the Society (P., 1914, 30, 302), the orientation of the nitro-group in nitrophenylselenious acid had not been determined, and in the discussion on the paper, Dr. Tuck suggested that the constitution of this acid might be settled by preparing the three isomerides by the action

of the nitrobenzenediazonium chlorides on potassium selenocyanate and suitable after-treatment. This method had already been applied by Bauer (*Ber.*, 1913, **46**, 92) to the preparation of *o*-nitrophenyl selenocyanate, and by Morgan and Elliot (*P.*, 1914, **30**, 248) to the preparation of *p*-chlorophenyl selenocyanate and their derivatives.

At the author's request, Mr. H. King has now kindly prepared *m*-nitrophenyl selenocyanate, from which he has obtained, on reduction with tin and hydrochloric acid, di-*m*-aminophenyl diselenide, identical with the product resulting from the reduction of nitrophenylselenious acid, thereby proving the constitution of the compounds described above.

#### EXPERIMENTAL.

##### *Phenylselenious Acid*, $\text{PhSeO}_2\text{H}$ .

The preparation of this acid and its nitrate have been described by Stoecker and Krafft (*Ber.*, 1906, **39**, 2197). Diphenyl diselenide (1 part by weight) was dissolved in concentrated nitric acid (40 parts by weight) and heated. On cooling, the well-crystallised nitrate of phenylselenious acid separated. In order to liberate the free acid, the nitrate was dissolved in ammonia and mixed with silver nitrate, when silver phenylselenite was precipitated, and gave the free acid when decomposed with the equivalent quantity of hydrochloric acid.

Doughty (*Amer. Chem. J.*, 1909, **41**, 326) subsequently obtained this acid by the action of hydrochloric acid on phenylselenic acid resulting from the interaction of selenic acid and benzene. He was unable to confirm the previous author's statement that the acid crystallised with  $2\text{H}_2\text{O}$ , finding it to be anhydrous.

For the purpose of the present investigation, considerable quantities of this acid were required, and a modification of Stoecker and Krafft's process was adopted. Instead of employing pure diphenyl diselenide, the mixture of this substance with selenophenol, obtained by the action of selenium on magnesium phenyl bromide (Taboury, *Bull. Soc. chim.*, 1903, [iii], **29**, 761), was used. On treating this with 4 c.c.—instead of 30 c.c.—of nitric acid for each gram, phenylselenious acid nitrate was readily prepared in quantity. When mixed with sufficient ammonia to neutralise the nitric acid, it gave free phenylselenious acid, which was found to be practically anhydrous, in agreement with Doughty's observation.

To a solution of magnesium phenyl bromide in dry ether, prepared from 24 grams of magnesium and 157 grams of bromo-

benzene, 79 grams of selenium were added gradually, and the mixture was boiled for half an hour. The product was decomposed with ice and dilute hydrochloric acid, well shaken, and the ethereal layer removed, the aqueous layer being extracted with ether twice again. The ethereal extracts were combined, dried with calcium chloride, and the solvent was removed on the water-bath. The resulting oil (about 130 grams) was then allowed to flow drop by drop into concentrated nitric acid (D 1.4), of which 4 c.c. were employed for each gram of the oil. The nitric acid solution was then digested for an hour on the water-bath and kept, when crude phenylselenious acid nitrate separated in hard crystals. This was collected on asbestos, dissolved in water, and the solution filtered from insoluble matter. The solution was then extracted with ether to remove further impurities, and evaporated to a syrup. On cooling, this set to a chalky mass of the nearly pure nitrate, which, after thorough drying in the air, amounted to about 110 grams. The yield is thus 44 per cent. of the theoretical.

For the preparation of the free acid, 10 grams of the nitrate were dissolved in 20 c.c. of water, and 6 c.c. of 10 per cent. aqueous ammonium hydroxide added. On stirring, phenylselenious acid separated in sandy, yellow grains, which were purified by crystallisation from water. 6.5 Grams of the pure acid were isolated without carrying out the separation to an end, whilst 7.6 grams are required theoretically. Phenylselenious acid, prepared in this way, melted at 124—125° (corr.) after drying at 100°. The air-dried acid was practically anhydrous. (Found, loss at 100°=0.4; C=37.6; H=3.3.  $C_6H_5SeO_2H$  requires C=38.0; H=3.2 per cent.)

*Sodium phenylselenite* crystallises from water in colourless plates containing  $2H_2O$ . It is readily soluble in water.

Found, loss at 100°, 14.6.

$C_6H_5SeO_2Na \cdot 2H_2O$  (247.2) requires  $H_2O=14.6$  per cent.

Found, in anhydrous salt, Se=37.9, 37.5.\*

$C_6H_5SeO_2Na$  requires Se=37.5 per cent.

#### *Salts of Phenylselenic Acid.*

Stoecker and Krafft (*loc. cit.*) prepared phenylselenic acid by the oxidation of diphenyl diselenide with moist chlorine, Doughty by the method given above (*loc. cit.*). The potassium salt can be obtained conveniently by oxidising phenylselenious acid with

\* For the estimation of selenium in the compounds described in this paper Frerichs's method (*Arch. Pharm.*, 1902, 240, 656) was employed.

potassium permanganate, removing manganese dioxide, and evaporating to low bulk, when it crystallises from the solution.

Potassium phenylselenate forms colourless, prismatic needles which, after being dried in the air, sinter from about 50° and melt from 65° to 90° in the water of crystallisation. It is readily soluble in cold, and very readily so in hot, water.

Found, loss in a vacuum over  $\text{H}_2\text{SO}_4$  and then at 100°, 12.7.

$\text{C}_6\text{H}_5\cdot\text{SeO}_3\text{K}\cdot 2\text{H}_2\text{O}$  (279.4) requires  $\text{H}_2\text{O}=12.9$  per cent.

Found, in anhydrous salt,  $\text{Se}=32.2$ .

$\text{C}_6\text{H}_5\cdot\text{SeO}_3\text{K}$  requires  $\text{Se}=32.6$  per cent.

Sodium phenylselenate was prepared from the barium salt, which has been described by Doughty (*loc. cit.*), by double decomposition with sodium sulphate. It crystallises from water in long, clear, oblong plates which contain  $3\text{H}_2\text{O}$ , and is readily soluble in cold, very readily so in hot water.

Found, in air-dried salt: loss at 120°=24.2;  $\text{Se}=26.5$ .

$\text{C}_6\text{H}_5\cdot\text{SeO}_3\text{Na}\cdot 4\text{H}_2\text{O}$  (299.2) requires  $\text{H}_2\text{O}=24.1$ ;  $\text{Se}=26.5$  per cent.

#### *m*-Nitrophenylselenious Acid, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SeO}_2\text{H}$ .

Phenylselenious acid did not yield a nitro-derivative when treated with a mixture of sulphuric and nitric acids at 100°. When subjected to the action of a large excess of fuming nitric acid at 150° for one hour, it gave a 20 per cent. yield of *m*-nitrophenylselenious acid. The best method for the preparation of this acid, however, was found in the action of nascent nitric acid generated from potassium nitrate.

Thirty grams of phenylselenious acid nitrate were dissolved in 30 c.c. of sulphuric acid, and the solution was cooled with running water. Twelve grams of finely powdered potassium nitrate were then stirred into the solution, which was similarly cooled. The mixture was heated for two hours in the steam-bath, and poured into 600 c.c. of water. After keeping for several hours, the separated crystals were collected. They amounted to 17.4 to 18.7 grams of an almost pure product melting at 155° or slightly lower.

*m*-Nitrophenylselenious acid crystallises from water in yellow, prismatic needles, which melt at 156–157° (corr.) after drying at 100°. It is fairly readily soluble in boiling water, sparingly so in cold.

Found, loss at 100°=0.4; in dried substance,  $\text{C}=30.8$ ;  $\text{H}=2.2$ .

$\text{C}_6\text{H}_3\text{O}_4\text{NSe}$  (234.2) requires  $\text{C}=30.8$ ;  $\text{H}=2.2$  per cent.

*m*-Nitrophenylselenic Acid,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SeO}_3\text{H}$ .

Thirty-five grams of *m*-nitrophenylselenious acid were dissolved in 600 c.c. of boiling water to which 20 c.c. of 10 per cent. aqueous potassium hydroxide had been added, and mixed with a solution of 16 grams of potassium permanganate in 200 c.c. of hot water. Further small quantities of permanganate were then added until the red colour no longer quickly vanished. The manganese dioxide was removed by filtration, and the solution evaporated to low bulk and cooled, when potassium *m*-nitrophenylselenate crystallised out. After purification by recrystallisation from water, 34 grams were obtained.

Potassium *m*-nitrophenylselenate forms hard, yellow rosettes of flat needles. It is anhydrous, and is readily soluble in hot, but somewhat sparingly so in cold, water. It explodes violently at about  $330^\circ$  (corr.).

Found: Se = 27.1.

$\text{C}_6\text{H}_4\text{O}_5\text{NKSe}$  (288.3) requires Se = 27.5 per cent.

Barium *m*-nitrophenylselenate was prepared from the potassium salt by double decomposition with the calculated quantity of barium chloride. It forms colourless leaflets which are fairly readily soluble in hot, but sparingly so in cold, water. It contains  $2\text{H}_2\text{O}$ , which are lost at  $120^\circ$ , but not at  $110^\circ$ .

Found, in air-dried salt, loss at  $120^\circ = 5.6$ . Ba = 20.2.

$\text{C}_{10}\text{H}_8\text{O}_{10}\text{N}_2\text{BaSe}_2\cdot 2\text{H}_2\text{O}$  (671.9) requires  $\text{H}_2\text{O} = 5.4$ ; Ba = 20.5 per cent.

*m*-Nitrophenylselenic acid was prepared from the barium salt by the addition of the calculated quantity of sulphuric acid, removal of barium sulphate, and evaporation to a syrup, when it crystallised, on keeping, in colourless plates containing  $2\text{H}_2\text{O}$ . The air-dried acid melts below  $100^\circ$ , but after drying first in a vacuum over sulphuric acid, then at  $100^\circ$ , it is rendered anhydrous and then melts at  $146^\circ$  (corr.).

Found, loss at  $100^\circ = 12.8$ .

$\text{C}_6\text{H}_5\text{O}_5\text{NSe}_2\cdot 2\text{H}_2\text{O}$  (286.3) requires  $\text{H}_2\text{O} = 12.7$  per cent.

0.2379, dried at  $100^\circ$ , required 18.95 c.c. of  $N/20\text{-NaOH}$  for neutralisation, whence equivalent = 251.

$\text{C}_6\text{H}_5\text{O}_5\text{NSe}$  requires M.W. = 250.3.

*Di-m-nitrophenyl Diselenide*,  $(\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{Se})_2$ .

Twenty-four grams of *m*-nitrophenylselenious acid were dissolved in 250 c.c. of boiling water, and a saturated solution of sodium

hydrogen sulphite was added so long as a turbidity was produced. After cooling and stirring, the oil which had separated became crystalline, and was collected and washed with water. The theoretical yield—20·5 grams—was obtained, and the product melted at 79°. After crystallisation from ether, this compound formed yellow spears which melted at 83° (corr.).

Found: C=35·6; H=2·2.

$C_{15}H_8O_4N_2Se_2$  (402·5) requires C=35·8; H=2·0 per cent.

It is insoluble in water, moderately readily soluble in cold alcohol or ether, fairly readily so in hot alcohol, and easily so in hot ether.

*Di-m-aminophenyl Diselenide*,  $(NH_2 \cdot C_6H_4 \cdot Se)_2$ .

Fifty grams of di-m-nitrophenyl diselenide were added to a solution of 300 grams of commercial hydrated sodium sulphide in 500 c.c. of 10 per cent. aqueous sodium hydroxide previously heated to about 60°, and the mixture was boiled for one hour under a reflux condenser. One litre of boiling water was then added, and an excess of concentrated hydrochloric acid. After digestion for two hours on the steam-bath, the separated sulphur was removed by filtration. The filtrate was cooled, basified with sodium carbonate, and extracted with ether. The ethereal solution was dried with anhydrous potassium carbonate and distilled. The residue was mixed with an excess of 10 per cent. hydrochloric acid, when 39·7 grams of di-m-aminophenyl diselenide dihydrochloride separated in sandy crystals.

*Di-m-aminophenyl diselenide dihydrochloride* crystallises from dilute hydrochloric acid in yellow grains formed of small needles. It melts and decomposes at 291—292° (corr.). It is readily soluble in hot, but sparingly so in cold, dilute hydrochloric acid.

Found, loss at 100°=1·1; in dried salt, C=35·3; H=3·5; Se=37·5; Cl=16·8.

$C_{12}H_{12}N_2Se_2 \cdot 2HCl$  (415·4) requires C=34·7; H=3·4; Se=38·1; Cl=17·1 per cent.

*Di-m-acetylaminophenyl Diselenide*,  $(CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot Se)_2$ .

25·2 Grams of di-m-aminophenyl diselenide dihydrochloride were converted into the base, and this was treated with 25 c.c. of acetic anhydride. The clear liquid quickly began to crystallise, and soon set to a yellow, chalky mass, which was washed well with ether and dried in the air. 19·6 Grams of di-m-acetylaminophenyl diselenide



melting at  $180^{\circ}$  were thus obtained, the yield amounting to 76 per cent. of the theoretical.

For the preparation of this substance, the previous isolation of di-*m*-aminophenyl diselenide as the dihydrochloride is unnecessary; thus 91 grams of di-*m*-nitrophenyl diselenide were reduced by the method given previously, and the ethereal residue of crude di-*m*-aminophenyl diselenide was mixed with 50 c.c. of acetic anhydride and treated as above. The resulting di-*m*-acetylaminophenyl diselenide melted at  $179^{\circ}$  and amounted to 76 grams, that is, 79 per cent. of the theoretical.

*Di-m-acetylaminophenyl diselenide* crystallises from glacial acetic acid in rosettes of short, yellow needles which melt at  $185-186^{\circ}$  (corr.). It is anhydrous, and is insoluble in hot or cold water, almost insoluble in hot or cold ether, readily soluble in hot alcohol or glacial acetic acid, but sparingly so in these solvents when cold.

Found: C=45.0; H=4.0.

$C_{16}H_{10}O_2N_2Se_2$  (426.6) requires C=45.0; H=3.8 per cent.

*Formation of Di-m-aminophenyl Diselenide by the Reduction of m-Nitrophenyl Selenocyanate.*

*m*-Nitroaniline (6.9 grams) was diazotised in dilute hydrochloric acid solution at  $0^{\circ}$ , and, after filtering from 1 gram of diazoamino-compound, the acidity of the solution to Congo paper was removed by the addition of 10 grams of sodium acetate crystals. Potassium selenocyanate (7.2 grams) dissolved in a little water was added slowly with stirring. There was a brisk evolution of nitrogen accompanied by the separation of a red oil. On washing with water, the latter gradually solidified, and was dissolved in ether to free it from selenium powder (0.6 gram). The ethereal solution was concentrated, again filtered from a small quantity of a viscous red oil, and finally evaporated to a syrup, which crystallised on stirring. The product consisted of transparent crystals embedded in a small quantity of a deep red gum. The yield of crude *m*-nitrophenyl selenocyanate was 7.2 grams, or 73 per cent. of theory.

The crude product (3.4 grams) was dissolved in hot alcohol (50 c.c.) and reduced by boiling for one hour with tin (3.5 grams) and hydrochloric acid (45 c.c.; 32 per cent.). On concentration under diminished pressure, the hot solution deposited an orange-yellow, granular, crystalline stannichloride (5.8 grams).

One gram of the stannichloride was dissolved in water, and the tin removed as sulphide. The solution, on concentration, gave two

successive separations of crystalline di-*m*-aminophenyl diselenide dihydrochloride, 0.2 gram and 0.25 gram, each melting at 278–280° (uncorr.). (Found: Cl=17.0. Calc.: Cl=17.1 per cent.) Di-*m*-aminophenyl diselenide dihydrochloride, obtained by the reduction of di-*m*-nitrophenyl diselenide, melted at the same temperature as did a mixture of the two. Moreover, both form a sparingly soluble, primrose-yellow stannochloride crystallising in microscopic needles, and a stannichloride which tends to separate as an oil from cold solutions, but in granular crystals from hot solutions.

Acetylation of the di-*m*-aminophenyl diselenide, prepared from *m*-nitrophenyl selenocyanate, gave di-*m*-acetylaminophenyl diselenide in short needles which melted at 183–185° (uncorr.), the acetyl derivative of the reduction product of di-*m*-nitrophenyl diselenide melting at the same temperature, whilst a mixture of the two showed no depression of the melting point.

*m*-Acetylaminophenylselenious Acid,  $\text{CH}_3\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SeO}_2\text{H}$ .

Ten grams of di-*m*-acetylaminophenyl diselenide were added with stirring in quantities of about 1 gram to 40 c.c. of nitric acid (D 1.4) kept at –6° to –3°. At first, the diselenide dissolved, giving a clear solution, but the separation of white crystals soon commenced, and increased on the further addition of this substance. The crystals were collected on asbestos, washed with concentrated nitric acid, and drained on porous porcelain. This substance melted at 146°, and was the nitrate of *m*-acetylaminophenylselenious acid. After grinding it with water, filtering, and washing with water, crude *m*-acetylaminophenylselenious acid, melting at 201°, remained undissolved. The product at this stage still contained nitric acid, and a portion, on boiling with water with the view of recrystallising it, readily oxidised. The whole was therefore dissolved in an excess of hot dilute ammonia (200 c.c.), treated with animal charcoal, filtered, and acidified with glacial acetic acid. On keeping, *m*-acetylaminophenylselenious acid crystallised in fine, colourless needles, which were collected, washed well with water, and dried in the air. The yield amounted to 8.5 grams of the pure acid.

*m*-Acetylaminophenylselenious acid crystallises from boiling water in short, slender, colourless needles, which begin to turn brown at about 200° and melt and decompose at 209° (corr.). It is sparingly soluble in hot, very sparingly so in cold, water.

Found: C=39.5, 39.5; H=3.7, 3.8.

$\text{C}_8\text{H}_7\text{O}_3\text{NSe}$  (246.3) requires C=39.0; H=3.7 per cent.

# 174 META-SUBSTITUTED AROMATIC SELENIUM COMPOUNDS.

*Sodium m-acetylaminophenylselenite* crystallises from water in microscopic needles. After drying in the air, this salt contains  $7\text{H}_2\text{O}$ , of which 4 are lost at  $100^\circ$  and the remainder at  $120^\circ$ . It is fairly readily soluble in cold and easily so in hot water.

Found: loss at  $100^\circ=18.2$ ; loss at  $120^\circ=32.2$ .

$\text{C}_8\text{H}_8\text{O}_3\text{NNaSe}, 7\text{H}_2\text{O}$  (394.4) requires  $4\text{H}_2\text{O}=18.3$ ;  $7\text{H}_2\text{O}=32.0$  per cent.

## *Salts of m-Acetylaminophenylselenic Acid,* $\text{CH}_3\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SeO}_3\text{H}.$

Fifty-five grams of *m*-acetylaminophenylselenious acid were dissolved in 70 c.c. of 10 per cent. ammonia and a litre of hot water, and mixed with a hot aqueous solution of 26 grams of potassium permanganate. After digestion for a few minutes on the water-bath, the slight excess of permanganate was reduced by means of alcohol. The solution was boiled, filtered from manganese hydroxide, and 28.5 grams of barium nitrate were dissolved in it. On evaporating to a small volume and keeping, barium *m*-acetylaminophenylselenate crystallised out. After recrystallisation from water, 48 grams of the pure salt were obtained. A considerable further quantity was subsequently isolated from the mother liquors.

*Barium m-acetylaminophenylselenate* crystallises from water in hard, colourless, flat needles containing  $4\text{H}_2\text{O}$ . It is fairly readily soluble in cold, very readily so in hot, water.

Found: loss at  $120^\circ=10.1$ .

$\text{C}_{16}\text{H}_{16}\text{O}_8\text{N}_2\text{BaSe}_2, 4\text{H}_2\text{O}$  (732.0) requires  $\text{H}_2\text{O}=9.8$  per cent.

Found, in dried salt,  $\text{Ba}=20.8$ .

$\text{C}_{16}\text{H}_{16}\text{O}_8\text{N}_2\text{BaSe}_2$  requires  $\text{Ba}=20.8$  per cent.

*Sodium m-acetylaminophenylselenate* was prepared from the barium salt by double decomposition with sodium sulphate. It crystallises from water in colourless, woolly needles, and from alcohol in prismatic needles, in both cases without solvent of crystallisation. It is very readily soluble in water, sparingly so in cold alcohol, but fairly readily so in hot alcohol.

Found:  $\text{Se}=27.9$ .

$\text{C}_8\text{H}_8\text{O}_4\text{NNaSe}$  (284.2) requires  $\text{Se}=27.9$  per cent.

## *m-Aminophenylselenic Acid,* $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SeO}_3\text{H}.$

Forty-five grams of barium *m*-acetylaminophenylselenate were dissolved in 500 c.c. of boiling water, and sufficient sulphuric acid

was added exactly to remove the barium. The solution was then boiled, filtered from barium sulphate, and evaporated to a small volume under diminished pressure, when 13 grams of *m*-aminophenylselenic acid crystallised from the solution.

*m*-Aminophenylselenic acid crystallises from water in colourless needles which contain  $2\text{H}_2\text{O}$ , and, after drying at  $100^\circ$ , melts and decomposes at  $229^\circ$  (corr.). It is readily soluble in hot, sparingly so in cold, water.

Found, in air-dried substance, loss at  $100^\circ = 11.4$ .

$\text{C}_6\text{H}_7\text{O}_3\text{NSe} \cdot 1\frac{1}{2}\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 10.9$  per cent.

Found, in dried substance, C = 32.7; H = 3.3.

$\text{C}_6\text{H}_7\text{O}_3\text{NSe}$  (220.3) requires C = 32.7; H = 3.2 per cent.

Sodium *m*-aminophenylselenate crystallises from water in plates, which are readily soluble in cold water.

Found, in air-dried salt, loss at  $120^\circ = 19.9$ .

$\text{C}_6\text{H}_6\text{O}_3\text{NNaSe} \cdot 3\frac{1}{2}\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 20.6$  per cent.

Found, in dried salt, Se = 33.0.

$\text{C}_6\text{H}_6\text{O}_3\text{NNaSe}$  (242.2) requires Se = 32.7 per cent.

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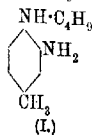
[Received, February 4th, 1919.]

### XX.—The *n*-Butylarylamines. Part III. Constitution of the Nitro-derivatives of *n*-Butyl-*p*-toluidine.

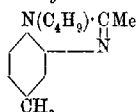
By JOSEPH REILLY and WILFRED JOHN HICKINBOTTOM.

IN Part II. of this series (T., 1918, 113, 985), the preparation of 2- and 3-nitro-*n*-butyl-*p*-toluidines was described, and in the present paper an account is given of the products of reduction of these nitro-compounds, the study of which has shown that the constitutions previously assigned to them are correct.

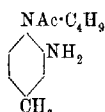
The 3-nitro-derivative, on reduction, furnishes 3:4-tolylene-4-*N*-*n*-butyldiamine (I), which is a readily oxidisable oil, and the corresponding 3-nitroacetyl derivative gives 2:5-dimethyl-1-*n*-butylbenzimidazole (II), which is also obtained by the action of heat on 4-acetyl-3:4-tolylene-4-*N*-*n*-butyldiamine (III).



(I.)



(II.)

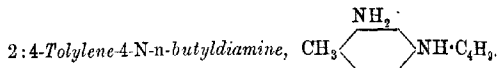


(III.)

The constitution of 3:5-dinitro-*n*-butyl-*p*-toluidine is proved by the fact that on hydrolysis with sodium hydroxide it yields *n*-butylamine and 3:5-dinitro-*p*-cresol.

By the action of acids or direct sunlight on 3:5-dinitro-*p*-tolyl-*n*-butyl-nitro- or -nitroso-amine, the dinitro-amine is regenerated and the nitroamine is similarly decomposed on boiling it with ethyl or *n*-butyl alcohols. When the nitroamine is hydrolysed by sulphuric acid or sodium hydroxide, nitrous acid is formed.

#### EXPERIMENTAL.



2-Nitro-*n*-butyl-*p*-toluidine (3 grams) was mixed with 10 c.c. of concentrated hydrochloric acid and 40 c.c. of water, and zinc dust (4 grams) gradually added. Excess of zinc was removed from the colourless solution, and the amine was isolated by the addition of sodium hydroxide solution, followed by extraction with ether. It formed a pale brown powder, which was purified by solution in dry ether and precipitation with light petroleum. A white, flocculent mass was obtained which, on drying, could easily be powdered. By spontaneous evaporation of the ethereal solution, it was obtained in colourless needles melting at 53°:

0.0956 gave 12.9 c.c.  $\text{N}_2$  at 19.2° and 750 mm.  $\text{N} = 15.56\%$ \*

$\text{C}_{11}\text{H}_{18}\text{N}_2$  requires  $\text{N} = 15.72$  per cent.

2:4-Tolylene-4-N-*n*-butyldiamine is soluble in most of the common organic solvents, sparingly so in water, and very sparingly so in light petroleum. With ferric chloride solution, it gives a very faint brown coloration, which, however, is not very characteristic. It gives no characteristic colour with nitrous acid or potassium ferrocyanide. The hydrochloride is very readily soluble in water.

4-Acetyl Derivative.—Tin foil was added to 2-nitroaceto-*n*-butyl-*p*-toluidine (1 mol) suspended in concentrated hydrochloric acid (6 mols.) until reduction was complete. The solution was filtered, diluted with water, and the tin removed by means of hydrogen sulphide. The filtrate was rendered alkaline and the amine isolated, as a brown oil, by extraction with ether. It solidified to a mass of brown crystals, which on crystallisation from a mixture

\* In the nitrogen estimations recorded in this paper, the gas was collected over 40 per cent. potassium hydroxide solution. A correction has been introduced for the vapour tension of the potassium hydroxide solution.

of ether and light petroleum was obtained in white crystals melting at 98–99°:

0.0723 gave 8.1 c.c.  $N_2$  at 20° and 749 mm.  $N=12.87$ .

$C_{13}H_{20}ON_2$  requires  $N=12.72$  per cent.

The compound dissolves in ether and many of the other organic solvents, but is insoluble in light petroleum. The diazo-compound gives with  $\beta$ -naphthol a brownish-red *azo-dye*, which dissolves in sulphuric acid with the development of a deep purple-red coloration, changing to pale brown on dilution. The *picrate* of the base crystallises from alcohol in groups of yellow needles melting at 185°.

### 3:4-Tolylene-4-N-n-butyl-diamine.

The reduction of 3-nitro-*n*-butyl-*p*-toluidine in the way described or the 2-nitro-compound, yields the corresponding diamine as an oil, which is white when first precipitated, but rapidly acquires a deep blue colour and ultimately becomes almost black:

0.1211 gave 16.2 c.c.  $N_2$  at 22° and 764 mm.  $N=15.57$ .

$C_{11}H_{18}N_2$  requires  $N=15.72$  per cent.

The compound is readily miscible with most of the ordinary organic solvents. The *hydrochloride* was obtained by passing a stream of dry hydrogen chloride into a solution of the base in dry xylene. The bulk of the xylene was decanted, and the rest removed by washing with light petroleum. After being dried at 100°, the salt formed a white powder. It is extremely deliquescent and very readily soluble in water:

0.0552 gave 0.0625 AgCl.  $Cl=28.0$ .

$C_{11}H_{18}N_2 \cdot 2HCl$  requires  $Cl=28.2$  per cent.

The aqueous solution is very readily oxidised. One drop of ferric chloride solution produces an intense blood-red or deep brown colour. A dilute solution of chromic acid or a very dilute neutral solution of potassium dichromate produces a brownish-black or black solution, depending on the concentration of the oxidising agent. An aqueous solution of bleaching powder yields a deep blue solution. Nitrous acid in dilute solution gives a dirty purple coloration, whilst concentrated nitric acid also gives a purple coloration.

The 3:4-*diacetyl* derivative was prepared by warming the base with acetic anhydride. A dark-coloured oil was obtained, which slowly solidified to a mass of dark brown crystals. By repeated crystallisation from a mixture of light petroleum and acetone, or

from hot dilute aqueous alcohol, it was obtained in white crystals melting at 130°:

0.0754 gave 7.1 c.c.  $N_2$  at 25° and 748 mm.  $N=10.62$ .

$C_{15}H_{22}O_2N_2$  requires  $N=10.69$  per cent.

The compound is moderately soluble in hot, but sparingly so in cold water.

#### 4-Acetyl-3:4-tolylene-4-N-n-butyl-diamine (III).

3-Nitroaceto-*n*-butyl-*p*-toluidide (4 grams) was dissolved in 50 c.c. of aqueous alcohol (70 per cent.) containing iron filings (10 grams), and to the mixture, warmed to 30°, glacial acetic acid was slowly added, the temperature being kept at 30°. After an hour, the mixture was heated on the water-bath, the unchanged iron removed by filtration, washed with warm dilute acetic acid, and the filtrate rendered alkaline and heated at 80° for several hours. The base was extracted with ether and purified by recrystallisation from a mixture of equal parts of dry ether and light petroleum, when it was obtained in short, colourless needles melting at 102°:

0.0702 gave 8.0 c.c.  $N_2$  at 21° and 738 mm.  $N=12.85$ .

$C_{15}H_{20}ON_2$  requires  $N=12.72$  per cent.

The compound is readily soluble in alcohol, ether, benzene, or carbon tetrachloride, but very sparingly so in light petroleum. The diazo-compound gives a red *azo-dye* with  $\beta$ -naphthol. On heating the base in a flask fitted with a short air condenser at 200° in an oil-bath, globules of water were observed in the condenser. After heating for four to five hours, the dark, viscous residue was distilled over a free flame, when a pale yellow oil was obtained which did not solidify at 0°, and was not a primary amine. From its method of formation, it is probably 2:5-dimethyl-1-*n*-butylbenzimidazole (II). The same compound was produced by the vigorous reduction of 3-nitroaceto-*n*-butyl-*p*-toluidide in acid solution.

The nitro-compound (5 grams) was dissolved in a mixture of glacial acetic acid (25 grams), concentrated hydrochloric acid (10 grams), and water (15 c.c.). Zinc dust (20 grams) was added, and the solution became very warm. After the reaction had moderated and more zinc dust had been added, the solution was heated on the sand-bath for one or two hours. After removal of the excess of zinc, the solution was rendered alkaline with potassium hydroxide solution, and the precipitated oil extracted with ether.

On distillation, it was obtained as a very viscous, pale yellow oil boiling at 335—338°:

0.0746 gave 0.2115  $\text{CO}_2$  and 0.0606  $\text{H}_2\text{O}$ .  $\text{C}=77.34$ ;  $\text{H}=9.09$ .

0.0794 „ 9.9 c.c.  $\text{N}_2$  at 23.1° and 736 mm.  $\text{N}=13.92$ .

$\text{C}_{18}\text{H}_{18}\text{N}_2$  requires  $\text{C}=77.18$ ;  $\text{H}=8.97$ ;  $\text{N}=13.85$  per cent.

2:5-Dimethyl-1-*n*-butylbenziminazole is miscible with ether or alcohol. When exposed in an open dish to a moist atmosphere, it readily absorbs water and oxygen, gradually becoming darker. By the action of an aqueous-alcoholic solution of picric acid on the alcoholic solution of the anhydro-base, the *picrate* was precipitated; this crystallised from acetone in short, yellow needles or prisms melting at 209°:

0.0756 gave 10.7 c.c.  $\text{N}_2$  at 21° and 749 mm.  $\text{N}=16.20$ .

$\text{C}_{18}\text{H}_{18}\text{N}_2\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$  requires  $\text{N}=16.24$  per cent.

It is practically insoluble in water, ether, or alcohol.

#### *Action of Alkalis on 3:5-Dinitro-n-butyl-p-toluidine.*

The dinitro-compound (1 gram) was heated under reflux with a solution of 5 grams of potassium hydroxide in 40 c.c. of water for six to eight hours. The colour of the solution changed rapidly through brownish-red to very dark red or almost black. On distillation into dilute hydrochloric acid, *n*-butylamine hydrochloride was obtained. The alkaline residue in the flask, after being cooled and filtered, was acidified with dilute sulphuric acid, and from the ethereal extract a solid crystallising in yellow needles (m. p. 82°) was obtained, which proved to be 3:5-dinitro-*p*-cresol.

#### *Action of Acids on 3:5-Dinitro-p-tolyl-n-butyl-nitroamine and -nitrosoamine.*

3:5-Dinitro-*p*-tolyl-*n*-butylnitroamine (0.5 gram) was dissolved in 2 c.c. of concentrated sulphuric acid (97 per cent.), the solution being kept cool by immersion in ice-cold water. The nitroamine dissolved slowly with the production of a deep reddish-purple colour, which changed finally to yellow. After half an hour, the mixture was poured on ice, when a yellow solid was obtained, which proved to be the corresponding nitrosoamine. Nitrous acid was also found to be present. In another experiment, 50 c.c. of slightly warmed sulphuric acid (90 per cent.) were added to the nitroamine (0.5 gram). There was a faint odour of nitrous acid, and the colour changes were the same as those described above.



After remaining for twenty days, exposed for part of the time to sunlight, the colour had changed to deep red. On pouring into water and extracting with ether, 3:5-dinitro-*n*-butyl-*p*-toluidine was obtained as the chief product. Further, the nitroamine (0.5 gram) was heated under reflux with a mixture of concentrated hydrochloric acid (20 c.c.) and *n*-butyl alcohol (50 c.c.) for eight hours. The colour of the mixture gradually became darker until it was finally a deep red. After removal of the alcohol, a red substance melting indefinitely at 65–80° was obtained. The melting point was raised to 86–88° by treatment with amyl nitrite in the presence of hydrochloric acid, the colour also becoming considerably paler.

On warming the nitroamine with an aqueous solution of perchloric acid and allowing the mixture to remain for twelve hours, a slight darkening occurred. The action of glacial phosphoric acid in the cold produced practically no colour change after a week.

3:5-Dinitro-*p*-tolyl-*n*-butylnitrosoamine, by the action of hydrochloric acid containing some aniline hydrochloride, yields the corresponding amine in almost quantitative yield and in a pure condition (compare Pinnow, *Ber.*, 1897, **30**, 838). The nitrosoamine (2.4 grams) was heated under reflux for eight hours with alcoholic hydrogen chloride (50 c.c.) containing aniline hydrochloride (1 gram). On evaporating the alcohol, 2.1 grams of 3:5-dinitro-*n*-butyl-*p*-toluidine, identified by the mixed melting-point method, were obtained. When the aniline hydrochloride was omitted, the reaction followed a similar course, but required a longer time for completion.

*Action of Alkalis on 3:5-Dinitro-p-tolyl-n-butyl-nitroamine and -nitrosoamine.*

Alcoholic potassium hydroxide reacts with alcoholic solutions of the nitroamine and nitrosoamine with the production of a dark purple colour, which gradually deepens in intensity. In aqueous solution, the reaction takes place much more slowly. 3:5-Dinitro-*p*-tolyl-*n*-butylnitrosoamine (1 mol.) was heated under reflux with a large excess of a 10 per cent. aqueous solution of sodium hydroxide (15 mols.). The nitroamine was slowly attacked, yielding a purple solution which gradually became almost black, when the reaction was considered to be complete. On distillation, *n*-butylamine was obtained. The alkaline residue in the flask, which contained sodium nitrite, was diluted, and, after filtering, rendered acid in the presence of carbamide to remove nitrous acid. On extraction

with ether, a pale brown oil was obtained, which solidified to a yellow, crystalline solid. After several crystallisations from aqueous alcohol, this melted at  $82^{\circ}$ , and was shown to be 3:5-dinitro-*p*-cresol.

When either the nitroamine or the nitrosoamine was heated with two or three times its weight of phenol at  $180^{\circ}$ , and the product treated with very dilute ice-cold sodium hydroxide solution, followed by extraction with ether, 3:5-dinitro-*n*-butyl-*p*-toluidine was obtained in good yield, and the same result was obtained by heating the nitroamine or nitrosoamine with a large excess of *n*-butyl alcohol or ethyl alcohol for several hours in diffused light.

Both the nitroamine and nitrosoamine were finely powdered and exposed in glass and quartz vessels to direct sunlight. After one hour, the nitrosoamine had deepened considerably in colour, and the melting point was depressed. The nitroamine, on the other hand, changed colour only slowly, but there was sufficient action in both cases after one month's exposure to detect the presence of 3:5-dinitro-*n*-butyl-*p*-toluidine. In some of the reactions where the decomposition was not complete, the melting point alone was not a sufficient guide to determine the composition of the product. The colour affords an indication of the production of the parent amine, and this was confirmed by the evidence obtained by the action of amyl nitrite and of nitric acid. In the decomposition of the nitrosoamine or of the nitroamine, the production of the parent amine was assumed to have occurred when the action of amyl nitrite or nitrous acid in the presence of hydrochloric acid or acetic acid effected a considerable loss of colour, and when the melting point was altered. The action of fuming nitric acid in giving a product identical with the original nitroamine showed that the butyl group had not been removed and that only the nitroso-group linked to the aminic nitrogen atom had been affected.

[Received, January 16th, 1919.]

XXI.—*Studies in Catalysis. Part X. The Applicability of the Radiation Hypothesis to Heterogeneous Reactions.*

By WILLIAM CUDMORE MCCULLAGH LEWIS.

In the previous papers of this series, the radiation hypothesis has been applied exclusively to reactions in homogeneous systems. A mode of applying the hypothesis to reactions in heterogeneous systems, including heterogeneous catalysis, having suggested itself to the author more than two years ago, it may not be out of place to indicate it briefly here.

In attempting to elucidate the mechanism of any chemical or physical process, two complementary methods of treatment may be employed. In the first, the process is considered from the point of view of the material or molecular changes involved; in the second, from the point of view of the concomitant or precedent energy exchanges. The radiation hypothesis belongs to the second method of treatment. The two methods are not distinct in the sense that the results obtained in one often furnish a clue to the solution of a difficulty met with in the other. It is necessary, however, to possess, in the first place, some information regarding the most probable material mechanism of the process considered before introducing considerations based on the energy exchanges involved. In the case of heterogeneous reactions and catalysis, Langmuir's theory of the spatial distribution of molecules and atoms at the interface between two phases will be adopted as a basis for the material changes occurring, the energy changes being then dealt with from the point of view of the radiation hypothesis.

Langmuir's theory (compare *J. Amer. Chem. Soc.*, 1916, 38, 2221) is essentially an extension of the work of the Braggs on crystal structure.

The surface of a solid is regarded as a checker-board on which atoms or molecules of gases may be condensed by being united to certain atoms in the surface itself. This adsorption effect is ascribed directly to valency, in some cases the surface being almost entirely covered or saturated, in others only a small fraction of the surface being thus occupied. According to Langmuir, this surface layer does not consist of several layers of molecules or atoms in which the density varies continuously. Instead, the change from solid to homogeneous gas is abrupt. This is based on the idea that it is only a layer one molecule or atom in thickness

which would be held sufficiently firmly to the surface, especially at the moderately high temperatures at which heterogeneous reactions proceed in general with measurable velocity. Langmuir's experimental results support this view in many cases. When a gas molecule strikes a surface, it is in general condensed. The rate at which it evaporates depends on the chemical or specific nature of the molecule and of the layer of atoms in the surface of the solid. Thus nitrogen, in which the atoms are already very completely saturated, possesses only a feeble external field of force, and in the *molecular* form, therefore, will be only slightly adsorbed.

Langmuir has found that hydrogen in the *atomic* form, produced by heating a wire in dry hydrogen at very low pressures, has a remarkable tendency to be adsorbed, this being regarded as due to the unsaturated affinity of the hydrogen atom. Langmuir has calculated that in this case the adsorbed layer of gas is just one atom in thickness. Oxygen is likewise easily adsorbed by metallic (tungsten) filaments. This adsorbed layer is exceedingly stable, and is evidently distinct from the formation of the compound  $\text{WO}_3$ , which volatilises easily in comparison. On Langmuir's view, the oxygen is retained on the surface in the atomic form. A molecule or atom which is strongly adsorbed is capable of displacing one which is feebly adsorbed. Hence addition of a strongly adsorbed gas—which in certain cases may be the resultant of the reaction—may cover the surface of a solid more or less completely, the surface being thereby "poisoned" with respect to a reaction in which the reactants are only feebly adsorbed. Langmuir has given several instances of such effects. The essential point for our present purpose is the dissociation, partial or complete, which many substances undergo into the atomic state on being condensed on surfaces, the cause of such dissociation being the localised valencies or lines of force which hold the atoms of the condensed substance to certain atoms of the surface of the solid.\*

So much for the nature of the material changes involved. We have now to see how far the radiation hypothesis may assist in extending this view of the mechanism of the process

In general, the velocity constants of heterogeneous reactions are characterised by possessing smaller temperature coefficients than those which are possessed by reactions in homogeneous systems. This means, on the basis of the considerations developed in earlier papers, that the critical increment in the heterogeneous process is

\* The catalytic effect of traces of moisture in the activation of molecules and atoms, and therefore possibly of surfaces, is not considered in the present paper. The facts hitherto recorded point to the conclusion that water is effective where ions are required to enable the reaction to proceed.

less than it would be for the same process occurring in the homogeneous system. This, in fact, appears to be the basis of the accelerating or catalytic effect of a given surface as viewed from the energy required to effect the chemical change.

It has already been shown that the reactivity of a substance depends on the magnitude of its critical increment, that is, the amount of energy which must be added per molecule or per gram-molecule, in excess of the average energy content, in order to bring the molecule into the active state.

The higher the critical increment, the smaller is the reactivity or rate of reaction of the substance. This increment is taken account of by the exponential term which appears in the velocity expression developed in previous papers. The term referred to is  $e^{-E/RT}$ , where  $E$  is the critical increment per gram-molecule,  $R$  the gas constant per gram-molecule, and  $T$  the absolute temperature. It is this quantity that governs the magnitude of the temperature coefficient of a reaction, and, as is evident, the greater the value of  $E$  the greater is the temperature coefficient.

Let us suppose that a given reaction occurs in a homogeneous system, the sum of the critical increments of the reactants being  $E_1$ , whilst the sum of the critical increments for the same reaction when a heterogeneous catalyst is present is  $E_2$ . Then  $E_1 > E_2$ . The ratio of the velocity constant in the presence of the catalyst to that when the catalyst is absent is given essentially by the ratio  $e^{-E_2/RT} / e^{-E_1/RT}$  or  $e^{(E_1 - E_2)/RT}$ . This is, in general, a large positive quantity; it may be referred to as the catalytic factor. Let us suppose that the process considered involves the dissociation of a gaseous molecule. If this occurs in the homogeneous phase, the critical increment is large, of the order of 50,000 to 100,000 calories per gram-molecule. This energy has to be supplied by absorption of the radiation present in the system, and the greater the amount of energy required the higher must be the temperature in order that a sufficient number of quanta of high frequency may be available. If, on the other hand, a catalyst is present which is capable of condensing or adsorbing the gas in the atomic form, then the energy required is essentially that of sublimation or de-sorption of the atomic resultants from the surface diminished by the energy of adsorption or condensation of the molecular reactant. Such effects are in general small, of the order 5000 to 10,000 calories per gram-molecule. Hence in this case the catalytic factor would be  $e^{(50,000 - 5000)/RT}$ , which for the temperature  $T = 1000^\circ$  would correspond with  $e^{22.5}$ , or  $10^{10}$  approximately. It is evident that the effect which we have been considering is of very great magnitude, and to this extent is in agreement with the known high efficiency

of heterogeneous catalysts. From the point of view of the energy changes involved, therefore, the action of a catalyst is to be ascribed to the substitution of relatively small energy terms of the nature of de-sorption or sublimation effects in place of true critical energies of activation or dissociation. In general, the problem is not so simple as the case just considered. Frequently more than one reactant is involved, and in some cases partial activation or polarisation of one or more of the reactants may be effected without such reactant coming into direct contact with the surface of the solid itself. This will naturally occur when the surface is already covered by a reactant which possesses high capacity of adsorption. In general, however, the function of the catalyst is to bring at least one of the reactants into the active form, which would otherwise only be attained in the homogeneous phase by exceedingly high temperature conditions. The possibilities which present themselves will be rendered somewhat clearer by a preliminary examination of one or two actual cases.

#### *The Reaction between Oxygen and Sulphur.*

We shall first of all consider the reaction,  $S + O_3 = SO_2$ , as occurring in the homogeneous gaseous state.

Since the resultant contains two atoms of oxygen, the process does not require complete dissociation of the oxygen molecule as a preliminary step. Instead, a partial activation or polarisation of the oxygen molecule is sufficient. A value for this quantity may be obtained from a consideration of the thermal decomposition of ozone, which has been measured by Chapman and Jones (T., 1910, 97, 2463), the reaction being shown to be bimolecular. The details of the calculation will be given in a subsequent paper, but it may be stated here that the critical increment of ozone per gram-molecule, obtained from Chapman and Jones's results, is 10,690 cal. Further, the heat evolved at constant volume when two gram-molecules of ozone decompose into three gram-molecules of oxygen has been determined with accuracy by Kailan and Jahn (*Zeitsch. anorg. Chem.*, 1910, 68, 243), the value being 69,000 cal. Applying the quantum expression (compare T., 1917, 111, 1086) to the process  $2O_3 \rightarrow 3O_2$ , we obtain  $69,000 = 3E'_{O_3} - 21,380$ , whence  $E'_{O_3} = 30,127$  cal., or 30,000 cal. in round numbers. The symbol  $E'$  denotes the critical increment per gram-molecule required for the partial activation or polarisation of oxygen which will permit three molecules thus activated to react to form two molecules of ozone. A molecule possesses, in general, different degrees or stages of activation, and this may not be the one required in the case of

the union of oxygen with sulphur. All partial activations are, however, small quantities compared with the activation required to cause complete dissociation of a molecule. So far as order of magnitude is concerned, the above value may be employed in this preliminary investigation.

We have now to consider the activation of sulphur vapour. In the temperature range  $200^{\circ}$  to  $500^{\circ}$ , the vapour of sulphur consists mainly of the molecular form  $S_8$ . Preuner and Schupp (*Zeitsch. physikal. Chem.*, 1909, **68**, 148) have measured the equilibrium of the reaction  $4S_6 = 3S_8$ . The mean value of the heat effect is 26,500 cals. This heat is absorbed in breaking down  $3S_8$  molecules to  $4S_6$  molecules. The same authors have obtained a fairly accurate value for the heat absorbed, namely, 58,000 cals., in the gaseous reaction  $S_6 = 3S_2$ . Hence the process  $\frac{1}{4}S_8 \rightarrow S_2$  requires an absorption of heat equal to 21,542 cals. We have now to consider the heat absorbed in the dissociation of  $S_2$  into the atomic state. Budde (*Zeitsch. anorg. Chem.*, 1900, **78**, 169) has measured, by an explosion method, the equilibrium of the reaction  $S_2 = 2S$ , in the gaseous state, over the temperature range  $2000^{\circ}$  to  $2500^{\circ}$ . The results do not lead to an accurate value for the heat effect. Budde takes the value 120,000 cals. per gram-molecule. Von Wartenberg (*Zeitsch. anorg. Chem.*, 1908, **56**, 320) estimates the heat effect to be 90,000 cals. approximately. It has been shown (compare T., 1918, **113**, 471) that the critical increment in the case of the dissociation of a molecule into atoms is connected with the heat absorbed by the relation  $-Q_v = E - \frac{1}{2}RT$ . At  $T = 2000^{\circ}$ , the value of  $E$  obtained from Budde's results is therefore 122,000 cals., but this is liable to considerable error. On the radiation hypothesis, this energy should be given by  $Nh\nu$ , where  $\nu$  is the frequency of the light absorbed,  $N$  the number of molecules in one gram-molecule, and  $h$  Planck's constant. Martens (*Ann. Physik*, 1902, [iv], **8**, 603) has calculated that sulphur should possess a band in the ultra-violet region at  $\lambda = 226 \mu\mu$ . The corresponding frequency is  $13.3 \times 10^{14}$ , and therefore  $Nh\nu$ , or the critical increment per gram-molecule, should be 125,550 cals. This is remarkably close to the value calculated from Budde's data. In fact, the agreement is partly accidental. It is probable that the value obtained from Martens's data is the more correct. It follows that the heat of dissociation of diatomic sulphur into the atomic state in a gaseous system is 123,000 cals. per gram-molecule. Hence the energy absorbed in the process  $\frac{1}{4}S_8 \rightarrow 2S$  is  $(123,000 + 21,540)$ , or 144,500 cals. in round numbers. As might be expected, the chief factor in the total energy change from  $S_8$  to atomic sulphur is the single process of dissociating the  $S_2$  molecules. The critical increment

required to produce two gram-atoms of sulphur in the gaseous state from the corresponding quantity of  $S_8$  molecules is 147,000 cals., and therefore the critical increment per gram-atom is 73,500 cals.

We have now to consider the formation of sulphur dioxide from oxygen and sulphur, the latter consisting of  $S_8$  molecules, the system being entirely gaseous. The partial critical increment of the oxygen is taken to be 30,000 cals. per gram-molecule. Hence the total critical increment of the system ( $S + O_2$ ) under the conditions stated is (73,500 + 30,000), or 103,500 cals. The heat of formation of sulphur dioxide from solid sulphur and gaseous oxygen is 69,400 cals. per gram-molecule (Berthelot) (compare Ferguson, *Proc. Nat. Acad. Sci.*, 1917, **3**, 371). The heat of vaporisation of sulphur is 12,000 cals. per gram-atom in round numbers. Hence the heat of formation of sulphur dioxide from its gaseous components is 81,400 cals. Employing the relation:

$$\text{Heat evolved} = E_{\text{resultants}} - E_{\text{reactants}}$$

we get  $81,400 = E_{SO} - 103,500$ , whence  $E_{SO} = 184,900$  cals. per gram-molecule. It follows from this value that the frequency of the effective radiation is  $19.6 \times 10^{14}$ , and the wave-length  $\lambda = 153 \mu\mu$ . Sulphur dioxide is known to have an absorption band in the extreme ultra-violet region beyond  $200 \mu\mu$  (compare Garrett, *Phil. Mag.*, 1916, [vi], **31**, 505), but the position of the band has not as yet been located.

The above exceedingly high value for the critical increment of sulphur dioxide requires that the molecule should be correspondingly stable. Thus it should not be possible to decompose it into its components by a quartz mercury lamp, since quartz does not transmit wave-lengths longer than about  $185 \mu\mu$ . As an illustration of its stability, it may be mentioned that von Wartenberg (*loc. cit.*) was unable to detect any sensible dissociation of sulphur dioxide even at  $2200^\circ$  abs. For our present purpose, it is more important to observe that the critical increment of the reactants ( $S + O_2$ ) is also very high, namely, 103,500 cals.

The numerical values given above refer to the reaction non-catalysed. If, however, the reaction is carried out in the presence of solid or fused sulphur, heterogeneous catalytic effects enter. This has been shown experimentally by Bodenstein and Caro (*Zeitsch. physikal. Chem.*, 1910, **75**, 30), the sulphur acting as a positive catalyst. The result of the positive catalysis is that the critical increment of the system ( $S + O_2$ ) is much less than the value given above. From the temperature coefficient obtained by Bodenstein and Caro in the region of  $250^\circ$ , in the presence of solid sulphur, it is found that the critical increment of the reactants



(S + O<sub>2</sub>) lies between the limits 31,308 and 34,184 cals., the mean value being 33,000 cals. in round numbers.

It is possible to account approximately for the order of magnitude of the critical increment obtained, when heterogeneous catalysis occurs, by supposing that the oxygen is already activated at the temperature chosen before coming into contact with the sulphur surface, the increment of partial activation of oxygen being of the order 30,000 cals., as we have seen already. The sulphur itself is already in the atomic state in the surface layer of the solid, and consequently does not require further activation. The heat of volatilisation of the sulphur dioxide per gram-molecule is a quantity of the order 5000 cals., so that in all the apparent increment is of the order 35,000 cals., which agrees moderately well with that observed.

In the above case, the catalytic factor at 250° is  $e^{(103,500 - 35,500)/RT}$  or  $e^{68,000/RT}$ , or  $10^{28}$  approximately. These numbers are simply employed for purposes of illustration; sufficient data have not yet been accumulated to permit of more exact calculation.

If such changes in the critical increment are brought about as a result of catalytic effects, it is necessary to conclude that in general the heat effect of a process will be modified by the catalyst, and if this is the case the variation of the equilibrium constant of the reaction in the surface layer with temperature will be affected, so that finally the equilibrium constant of the catalysed reaction will differ from that of the non-catalysed reaction. This conclusion is in general agreement with that arrived at by Bancroft (*J. Physical Chem.*, 1917, **21**, 573) on false equilibria and the effect of heterogeneous catalysis on the position of the equilibrium.

#### *The Union of Oxygen and Hydrogen.*

Bodenstein (*Zeitsch. physikal. Chem.*, 1899, **29**, 665) has found that the temperature of the termolecular velocity constant, corresponding with the reaction  $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ , is 1.75 for 10° over the temperature range 482° to 509°. The reaction proceeds under the conditions employed almost entirely at the surface of the porcelain containing-g-vessel. From the above value of the temperature coefficient, it would follow that the critical increment for two gram-molecules of hydrogen and one gram-molecule of oxygen is 66,000 cals., and therefore for one gram-molecule of hydrogen and one half-gram-molecule of oxygen the increment of the reactants is 33,000 cals. Bodenstein's results have, however, been criticised by Bone and Wheeler (*Phil. Trans.*, 1906, [A], **206**, 1), who find that the reaction is not termolecular, but approximately unimole-

ular, especially unimolecular with respect to the hydrogen. The reaction which appears to occur is therefore  $\text{H}_2 + \text{O} = \text{H}_2\text{O}$ . Bone and Wheeler have given data for the reaction from which the temperature coefficient and critical increment of the reactants may be calculated when nickel is the catalyst. For the temperature range  $473^\circ$  to  $493^\circ$  abs., the critical increment of the reactants is calculated to be 35,000 cal., which agrees fairly well with the value obtained from Bodenstein's results for the porcelain surface. Over the temperature range  $493^\circ$  to  $513^\circ$  abs., the results obtained by Bone and Wheeler give an increment of 52,000 cal. in round numbers. This is considerably greater than that obtained at the lower range of temperature, and indicates that the catalytic effect is relatively less efficient at the higher temperature, due, presumably, to diminished adsorption of the reactants. In both cases, however, the increment is a relatively small quantity, very much smaller than would be expected from the process occurring in the homogeneous phase, for the molecule of oxygen, which has to be dissociated, is very stable.

We have now to attempt to account for a quantity of the above order of magnitude on the basis of the energy-mechanism outlined. Let us assume, in the first place, that the oxygen is adsorbed and exists in the atomic state attached to certain positions on the surface of the catalyst. It is necessary that an activated or polarised molecule of hydrogen shall come into contact with an oxygen atom. It is only necessary for the hydrogen to be partly activated. Bohr (*Phil. Mag.*, 1913, [vi], **26**, 1, 476, 357) has investigated the energy changes which occur in the molecule and the atom of hydrogen in various processes involving the removal and addition of an electron. Bohr has calculated that the process of transferring an electron so as to give rise to a system consisting of a positively charged hydrogen atom and a negatively charged one requires an absorption of energy of 21,000 cal. per gram-molecule of hydrogen. We shall employ this value in the present case, although there is evidence that a somewhat higher value is probably more correct. The latent heat of vaporisation of water is in round numbers 9000 cal. per gram-molecule in the neighbourhood of  $100^\circ$ . As before, we shall assume that the heat of desorption of the water produced in the reaction is of the same order of magnitude. Hence we would expect the critical increment of the process to be of the order 30,000 cal. per gram-molecule of hydrogen and per gram-atom of oxygen. This agrees moderately with the observed value.

Sufficiently accurate data are not as yet available for calculating the critical increment of the reactants of the same reaction in the

homogeneous gaseous state. It is necessary to dissociate the molecule of oxygen, and this appears to require a quantum of energy corresponding with approximately the region  $\lambda=200\mu$ , whence the critical increment per gram-molecule is of the order 140,000 to 150,000 cals. That is, the total increment of the reactants, reckoned per gram-molecule of hydrogen, is  $21,000 + 140,000/2$ , or 91,000 cals. The catalytic efficiency is therefore given by the ratio  $e^{-33,000/RT}/e^{-91,000/RT}$  or  $e^{58,000/RT}$ . At  $500^\circ$  this factor is of the order  $10^{17}$ . These figures are merely illustrative, but they serve to indicate the great influence on the velocity which is to be expected on the basis of the treatment suggested.

In dealing with the union of oxygen and hydrogen, it has been assumed above that the oxygen is condensed in the atomic form on the catalyst, the subsequent chemical change being  $H_2 + O = H_2O$ . From a number of observations made by Bone and Wheeler (*loc. cit.*), it appears that hydrogen is preferentially adsorbed. In such cases, the most probable reaction, because it involves the minimal critical increment, would be represented by  $H_2 + O_2 \rightarrow H_2O_2$ , in which the hydrogen and oxygen are partly activated, but neither of them is completely dissociated. The formation of water would result from the subsequent decomposition of the hydrogen peroxide. The idea that hydrogen peroxide is an intermediate stage is, of course, not new. It appears from such considerations that the specific nature of the catalyst may determine the actual mechanism of a given reaction to a large extent.

#### *The Union of Oxygen and Silicon.*

In the reactions just considered, the critical increment of partial activation of oxygen has been taken to be 30,000 cals. approximately, this being the value required for the formation of ozone. As already pointed out, more than one stage of activation may be anticipated up to the limiting activation which corresponds with complete dissociation of the molecule into atoms. Each activation corresponds with a certain size of quantum of radiant energy, that is, with a certain frequency. The general conclusion reached in connexion with absorption spectra is that frequencies are related to one another in terms of even multiples of some fundamental frequency, that is, various degrees of activation are similarly related. A low degree of activation of the oxygen molecule requires 30,000 cals. of energy to be absorbed per gram-molecule, and therefore higher degrees of activation would require 60,000, 90,000 cals., etc., up to the limiting value of complete dissociation, which

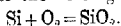
appears to correspond with a quantity of the order 140,000 to 150,000 cals.

Sufficient information is not as yet available to enable us to say how many of these possible degrees of activation may actually manifest themselves. As an example of partial activation of oxygen which is apparently considerably greater than 30,000 cals., we may take the case of the formation and decomposition of an exceedingly stable compound, silica or quartz.

To decompose a molecule of quartz, it is evident that a quantum in the very extreme ultra-violet portion of the spectrum is required, in order to supply the necessary energy. It is well known that quartz commences to absorb radiation sensibly beyond the wave-length  $185\ \mu\mu$ . S. Richardson (*Phil. Mag.*, 1916, [vi], **31**, 463) finds that the dispersional wave-length of quartz is  $105\ \mu\mu$ . It does not necessarily follow that the dispersional wave-length or frequency is that required for complete dissociation of the molecule. That in the case of quartz, however, the necessary wave-length cannot differ much from  $105\ \mu\mu$  is rendered probable by the following consideration. In a quartz mercury vapour lamp, it is generally believed that the quartz remains undecomposed; otherwise it would be difficult to account for the life and permanence of the lamp. That is, quartz can only be decomposed by a wave-length which is shorter than any emitted by the mercury vapour. O. W. Richardson and Bazzoni (*Phil. Mag.*, 1917, [vi], **34**, 285) have found that there is a limiting wave-length in the spectrum of a substance; that is, no wave-length shorter than a certain value, characteristic of the substance, can be emitted. In the case of mercury vapour, this limiting wave-length lies between 120 and  $100\ \mu\mu$ . The mean of these two limits is  $110\ \mu\mu$ , and we conclude on the above reasoning that quartz can only be decomposed by a wave-length shorter than this value. This points fairly definitely to S. Richardson's value,  $105\ \mu\mu$ , for the dispersional wave-length of quartz as being the wave-length capable of decomposing the molecule.

The critical increment corresponding with  $\lambda = 105\ \mu\mu$  is 270,000 cals. per gram-molecule of quartz, an enormous quantity, which is in qualitative agreement with the known stability of quartz.

We have now to consider the heterogeneous reaction



On Langmuir's view as applied in the present paper, we regard the silicon as already in the atomic state. If  $x$  is the necessary critical increment of oxygen per gram-molecule, then  $x$  is likewise the total critical increment of the reactants. The heat of the reaction is known to be 184,000 cals. in round numbers, and hence,

on applying the quantum-heat expression: heat evolved = critical increment of resultants - critical increment of reactants, we obtain  $184,000 = 270,000 - x$ , whence  $x = 86,000$  cal. Owing to the error in the observed heat effect and in the value of the critical increment of quartz, this value for the critical increment of oxygen may be regarded as agreeing approximately with the value 90,000 cal. expected from the lower degree of activation of the molecule. What is particularly important is that even this value does not correspond with complete dissociation of the oxygen molecule. We may therefore conclude that the molecule of quartz

possesses the structure  $\text{Si} \begin{array}{c} \diagup \text{O} \\ \diagdown \end{array}$ , rather than  $\text{O}:\text{Si}:\text{O}$ . This is an illustration of how a knowledge of the necessary critical increments—which in the present case, unfortunately, are not known with precision—may lead to information concerning molecular structure.

One of the chief difficulties met with in the kinetics of heterogeneous reactions has its origin in the selective nature of the adsorbability of the reactants and the resultants, particularly the latter. The so-called catalytic "poisons" are now generally regarded as owing their effect to marked selective adsorption, as a result of which the surface of the catalyst becomes covered with a layer of molecules, and is thus no longer capable of catalysing the reaction. In many cases, the resultants of the reaction are adsorbed in this manner, and consequently function as a catalytic poison. Since the extent of adsorption diminishes as the temperature rises, it is obvious that when such poisoning effects are present the temperature coefficient of the reaction velocity over a certain range of temperature is not comparable with that over a different range, for the total observed velocity depends not only on the true effect of temperature on the chemical process itself, but likewise on the alteration in the extent of active surface presented to the reactants. The simplest conditions are obviously those in which the adsorption effects are a minimum, and such conditions will occur generally when the energy required for sublimation or desorption is small. In the other cases where adsorption effects are large, it is necessary to correct the observed velocity constants for the change in the area of the effective surface produced as a result of the change in temperature. Thus in the case in which the resultant is markedly adsorbed, and therefore acts as a negative catalyst, the temperature coefficient will possess too high a value, and instead of decreasing as temperature rises, may even increase. A similar abnormal behaviour is to be anticipated when a reaction proceeds partly in the homogeneous gaseous phase, partly in the

surface, for as the temperature rises the reaction tends to predominate in the gaseous phase, and therefore possesses a higher temperature coefficient.

MUSPRATT LABORATORY OF PHYSICAL AND ELECTRO-CHEMISTRY,  
UNIVERSITY OF LIVERPOOL.

[Received, January 22nd, 1919.]

## XXII.—*The Estimation of the Methoxyl Group.*

By JOHN THEODORE HEWITT and WILLIAM JACOB JONES.

SINCE the introduction of the Zeisel method for the estimation of methoxyl groups (*Monatsh.*, 1885, **6**, 989; 1886, **7**, 406; Benedikt and Grüssner, *Chem. Zeit.*, 1889, **13**, 872), numerous attempts have been made to simplify the apparatus and shorten the operation. The method of rectifying the methyl iodide proposed by Zeisel is effective but troublesome; the inclined condenser has to be of considerable length, and consequently occupies some bench space, whilst the constant supply of water to the condenser at about 50° necessitates supervision. A further inconvenience of the Zeisel method is the trouble experienced in working up the precipitate of double iodide and nitrate of silver, time being lost in evaporating the alcohol and obtaining the silver iodide in a pure condition.

The use of a rectifying column provided with a thermometer, in place of the inclined condenser fed with water at an approximately definite temperature, was recommended by Hewitt and Moore (*T.*, 1902, **81**, 318), and impurities in the hydriodic acid were removed by passing carbon dioxide through the acid at 130° before introducing the substance under examination. Considerable saving in bench space was effected, and during the operation it was only necessary to control the stream of carbon dioxide and the flame under the glycerol bath so as to give the necessary temperatures in the reaction flask and at the top of the rectifying column. Several modifications of the Zeisel method have been suggested in which ordinary rectification has been relied on in place of inclined condensers in which the temperature is controlled by running water (Perkin, *T.*, 1903, **83**, 1367; Zeisel and Fanto, *Zeitsch. anal. Chem.*, 1903, **42**, 549; Stritar, *ibid.*, 579; Hesse, *Ber.*, 1906, **39**, 1142). Shortening the process by estimation of the methyl iodide in a more rapid manner was left untouched for years. The necessity of estimating methyl iodide obtained from methyl alcohol

mixtures rapidly and accurately caused the present authors to search for a quick process.

Since combination of alkyl iodides with bases of the pyridine series takes place very rapidly, there seemed to be a promising way of obtaining the iodide in an ionisable form and then estimating it volumetrically. After working out a satisfactory process, it was found that the same fundamental idea of combining the methyl iodide with a tertiary base had already been utilised (Kirpal and Bühn, *Ber.*, 1914, **47**, 1084), but the subsequent volumetric estimation of iodide by standard silver nitrate solution may be considerably shortened. Instead of rejecting the excess of pyridine by evaporation and estimating the iodide with standard silver nitrate, using a chromate as indicator, the pyridine and its methyl iodide may be directly diluted with water, acidified with nitric acid, a known amount of silver nitrate added, and the excess of the latter determined by thiocyanate according to Volhard's method. Adoption of this procedure reduces the time of experiment considerably.

The applicability of Volhard's method to the estimation of methyl iodide after reaction with pyridine was controlled in a separate experiment. 3.10 Grams of freshly distilled methyl iodide were diluted to a volume of 100 c.c. with pyridine which had been saturated with carbon dioxide. By dilution with water, addition of silver nitrate, and determination of the excess of silver with thiocyanate, 3.13 grams of methyl iodide per 100 c.c. were found.

#### *Method.*

*Hydriodic Acid.*—The hydriodic acid is prepared by saturating an aqueous suspension of iodine with hydrogen sulphide, distilling the resulting solution, and collecting the fraction boiling between 123° and 127° (D 1.7) for use.

Residues from analyses are redistilled and used again.

*Pyridine.*—Complete separation from picoline is unnecessary; it is, however, advisable to remove substances of high boiling point.

Pyridine bases as obtained from tar distillers are mixed with two-thirds of their weight of water and fractionated. The fraction distilling between 93° and 97°, containing the mixture of constant boiling point, is shaken with one-third of its weight of solid sodium hydroxide, the upper layer is separated, fractionally distilled, and the bases distilling between 114° and 117° are collected for use. Residues containing pyridine may be accumulated, rendered alkaline with one-fiftieth of their weight of solid sodium hydroxide, distilled, the distillate at 93—97° collected, and worked up.

*The Estimation.*—The apparatus consists of the usual carbon dioxide generator, decomposition flask heated in a glycerol bath to  $130^{\circ}$ , and rectifying column (four-pear or other suitable form). The carbon dioxide carrying the methyl iodide vapour is passed through two test-tubes in series, each containing 10 c.c. of pyridine.

For the estimation, a suitable weight of the substance is taken, and 20 c.c. of hydriodic acid (D 1.7) are added.

After the experiment has been in progress for one hour, the contents of the test-tubes are completely washed into a graduated flask, when they are diluted with water, and the iodide is estimated by the process indicated above.

In all cases, early in the course of the experiment, a yellow coloration develops in the pyridine. This vanishes on diluting the pyridine at the end of the experiment. Its appearance, therefore, need cause no apprehension to the analyst that free iodine is finding its way into the pyridine. Moreover, carefully purified samples of methyl iodide and pyridine on admixture develop colour. The behaviour of a mixture on dilution with water was compared with that of an iodine solution of equal depth of colour. On diluting a 3 per cent. solution of methyl iodide in pyridine with a quarter of its volume of water, the colour became very pale, and with its own volume of water it almost vanished. The iodine solution, on being similarly diluted, still retained its colour. It would thus appear that the coloration is not due to free iodine. Should, however, the colour persist on dilution with water, it is then advisable to discharge it with thiosulphate solution.

#### *Analyses.*

Substance.	Percentage of methoxyl group	
	Found.	Calculated.
Brucine hydrate .....	13.5	13.3
Methyl oxalate .....	50.1	52.5
Methyl alcohol .....	95.2	96.9
" " .....	95.2	96.9
" " .....	96.0	96.9
" " .....	96.3	96.9
Methyl salicylate .....	19.7	20.4

A methylated cellulose which gave 39.1 per cent. of methoxyl by the gravimetric Zeisel method was found to contain 39.2 per cent. by the present method.

Unsatisfactory results were obtained with a sample of methyl benzoate and with one of hydrated quinine sulphate.

This comparatively rapid method for the estimation of methoxyl



groups may be applied conveniently to the products of wood distillation or other mixtures containing methyl alcohol.

Methyl alcohol has usually been estimated in these products by conversion into methyl iodide, and measurement of the volume of the latter compound (Krell, *Ber.*, 1873, 6, 1310; Grodzky and Krämer, *ibid.*, 1492). Zeisel and Stritar's process of weighing volatilised iodine as silver iodide obviates the inexactness due to determination of the volume of the methyl iodide, but time may be saved by combining the methyl iodide with a tertiary base and estimating the iodine volumetrically.

A suitable amount (see below) of the liquid to be analysed is heated with 20 c.c. of hydriodic acid (D 1.7) for one hour. The contents of the test-tubes are then completely washed into a graduated flask and made up with water to 100 c.c. An aliquot portion (see below) of the diluted solution is introduced into a glass stoppered bottle of 250 c.c. capacity, 70 c.c. of water are added, and then, in order, 25 c.c. of *N*/10-silver nitrate solution and 30 c.c. of approximately 10*N*-nitric acid. The bottle is well shaken by hand for five minutes, and 5 c.c. of concentrated ferric alum indicator are added. *N*/10-Thiocyanate solution is now run in until further addition of one drop imparts a permanent orange colour to the liquid.

Suitable amounts of liquids to be taken for analysis are given below.

*a* represents the volume of material to be operated on and its dilution when necessary.

*b* gives the volume of the diluted aqueous pyridine solution, obtained as described above, to be actually used in a titration.

*c* is the formula to be used giving the weight in grams of methyl alcohol in 100 c.c. of the liquor analysed, where *t* is the number of c.c. of *N*/10-thiocyanate solution used in the titration. (*Note*.—The figure 25 given in the formulæ must be multiplied by *f*, the factor for the silver nitrate solution, if this is not exactly decinormal.)

*Pyroligneous Acid*.—(*a*) Take 5 c.c. of the original liquor; (*b*) 40 c.c.; (*c*) 0.16 (25—*t*).

*Crude Wood Naptha*.—(*a*) Take 10 c.c., dilute to 100 c.c. with water, and use 5 c.c. of the diluted solution for distillation with hydriodic acid; (*b*) 40 c.c.; (*c*) 1.6 (25—*t*).

*Methyl Alcohol and Mixtures of the Alcohol with Acetone*.—(*a*) Take 10 c.c., dilute to 100 c.c. with water, and use 5 c.c. of this diluted solution for the estimation; (*b*) 20 c.c.; (*c*) 3.2 (25—*t*).

*Analyses.*

Artificial mixtures containing methyl alcohol and other products of wood distillation were made up and analysed by the method described.

Liquor Number.	Composition. No. of grams of methyl alcohol per 100 c.c. of liquor.	
	Actual.	Found.
1 .....	2.39	2.35
2 .....	68.51	68.1
3 .....	2.39	2.35
4 .....	31.8	31.5

Analyses of purified methyl alcohol by the present method have already been given.

It will be seen that, on an average, the results are 1 per cent. too low. Stritar and Zeidler (*Zeitsch. anal. Chem.*, 1904, **63**, 387) found that the maximum amount of methyl iodide obtainable from pure methyl alcohol in a Zeisel estimation corresponded with a 99 per cent. yield.

Liquors 1 and 2 were aqueous solutions of purified methyl alcohol. Liquor 3 contained, per 100 c.c., 7.03 grams of acetic acid, 0.80 gram of acetone, and 2.39 grams of methyl alcohol, the remainder being water. It represented a pyroligneous acid. Liquor 4 was an equilibrium mixture prepared from 10.04 grams of acetic acid, 39.60 grams of acetone, and 31.82 grams of methyl alcohol, made up to 100 c.c. with water (1.27 grams). This mixture, which, of course, contained methyl acetate, represented the first runnings obtained in the rectification of crude wood naphtha.

*Compounds yielding Methyl Iodide, other than Methyl Alcohol,  
present in Wood Distillates.*

The constituents of wood distillates have been examined by Stritar and Zeidler (*loc. cit.*) with a view to determine which yield methyl iodide on treatment with hydriodic acid. They found that acetone gave no methyl iodide, whilst the yield from both formaldehyde and acetaldehyde was negligible. Methyl acetate gave one equivalent of methyl iodide, and methylal and dimethylacetal each gave two. Allyl alcohol yielded its equivalent of *sec.*-propyl iodide. Guaiacol and other methyl derivatives of the phenols yielded their equivalent of methyl iodide.

Of these substances, the quantities of acetal encountered are too

small to be of consequence. According to Grodzki and Krämer (*loc. cit.*), the amounts of allyl alcohol and of methyl alcohol in raw wood spirit are in the ratio of 2 to 1000. Stritar and Zeidler find that guaiacol may be eliminated from aqueous solutions of crude wood spirit by shaking with animal charcoal. They state that on omitting this treatment, the amount of methyl alcohol found is too high by about 2 parts in 100 parts. It will be seen that the quantities of alkyl iodide yielded by the amounts of allyl alcohol and of guaiacol present in the aqueous wood distillates, relatively to that yielded by the methyl alcohol present, border closely on the experimental error. It is the experience of the authors that, where precautions are taken to eliminate these substances preliminary to analysis, the errors due to losses outweigh the error introduced through ignoring their presence.

The present method gives the total methyl alcohol, including both the free alcohol and that which is combined as methyl acetate. If it is desired, the amount of ester present may be determined by quantitative hydrolysis.

The alcoholic silver nitrate of the Zeisel method of estimating methoxyl may be replaced by pyridine. The pyridinium methyl iodide formed can be determined by Volhard's thiocyanate method.

Methyl alcohol in wood distillates may be determined by the method described above.

[Received, January 17th, 1919.]

### XXIII.—*The Preparation of Monomethylaniline.*

By PERCY FARADAY FRANKLAND, FREDERICK CHALLENGER, and  
NOEL ALBERT NICHOLLS.

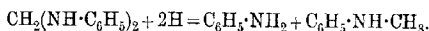
WHEN aniline is submitted to the action of the usual methylating agents, it is difficult to limit the course of the reaction to the introduction of a single methyl group. We have investigated the production of monomethylaniline by three methods, with a view to obtain it in a pure condition.

(1) The process described in the German Patent 75854, and with slight modifications in the French Patent 212506, consists in condensing aniline with formaldehyde and then reducing with zinc dust and concentrated aqueous sodium hydroxide until a test portion dissolves to a clear solution in acetic acid. Any unreduced methylenedianiline,  $\text{CH}_2\text{:N}\cdot\text{C}_6\text{H}_5$ , is thereby converted into insoluble

anhydroformaldehydeaniline,  $(\text{CH}_2\cdot\text{N}\cdot\text{C}_6\text{H}_5)_3$ . Using 100 grams of aniline, we have found the reduction to be completed in twelve to fifteen hours, and have obtained about 55 per cent. of the theoretical yield of methylaniline. The Patent Specifications make no mention of the yields obtained.

The principal advantage of this method lies in the fact that the product, although rich in aniline, contains only traces of dimethylaniline. The presence of the aniline may be the result of incomplete condensation with formaldehyde in the first instance, or of the hydrolysis of the methyleneaniline by the hot water, or of both causes. The primary base can be recovered in the form of its zincchloride, which is almost insoluble in water, the methylated bases not being affected by this reagent (*Monatsh.*, 1888, 9, 514). The method appears to work very satisfactorily.

Morgan (English Patent 102834), who has also studied the reduction of methyleneaniline, suggests that the poor yield of methylaniline may be due, in addition to hydrolysis, to the conversion of some of the methyleneaniline into *s*-diphenylmethylenediamine,  $\text{CH}_2(\text{NH}\cdot\text{C}_6\text{H}_5)_2$ , and anhydroformaldehydeaniline. We have failed to obtain more than traces of monomethylaniline from the last-named substance (compare, however, Goldschmidt, *Chem. Zeit.*, 1904, 28, 1229), but when *s*-diphenylmethylenediamine (Eberhardt and Welter, *Ber.*, 1894, 27, 1804; Eibner, *Annalen*, 1898, 302, 349) is reduced with zinc dust and alkali hydroxide under the conditions of the earlier patents, aniline and monomethylaniline are produced in equal amounts, probably according to the equation



We attempted to diminish the hydrolysis by performing the reduction in concentrated alcoholic solution. The yield of methylaniline was, however, only about 46 per cent. No better results were obtained by increasing the quantity of formaldehyde; 1.5 molecular proportions gave rise to some dimethylaniline, whilst with 10 molecular proportions, considerable quantities of this base were formed.\*

This appears to be due to the interaction of monomethylaniline and formaldehyde, giving rise to *s*-diphenyldimethylmethylenediamine, which then undergoes reduction. This reaction would, moreover, be analogous to the reduction of *s*-diphenylmethylenediamine. The condensation product of formaldehyde and methyl-

\* Compare the action of formaldehyde on methylaniline in acid solution (Goldschmidt, *loc. cit.*) and on methyl-*o*-toluidine (Braun, *Ber.*, 1908, 41, 2153), also on ammonium chloride (Werner, *T.*, 1917, 112, 844). See also Finnow, *Ber.*, 1894, 27, 3166; Cohn, *Chem. Zeit.*, 1900, 24, 564.

aniline (Braun, *Ber.*, 1908, 41, 2147) was therefore prepared and reduced under the usual conditions, with the result that much dimethylaniline was produced.

(2) The process described in various works of reference consists in heating aniline hydrochloride with methyl alcohol in an autoclave to 180–200°.\* The best result obtained by us in a series of thirteen experiments was a 55 per cent. yield of monomethylaniline. Experiments in sealed tubes confirmed these results.

We have also investigated a variation of the above method, in which aniline hydrochloride and methyl alcohol are heated together in the presence of glacial acetic acid (*Ber.*, 1897, 30, 3072). The most favourable result was a yield of 56 per cent. of methylaniline.

(3) The demethylation of dimethylaniline by heating with aniline hydrochloride at above 180°. In the most favourable experiments, a yield of 55 per cent. of methylaniline was obtained. Aniline was also heated to a high temperature with dimethylaniline hydrochloride with similar results, but it was found necessary to heat for a much longer period. This was probably due to the more basic nature of dimethylaniline. A condition of equilibrium between the three bases and hydrochloric acid would appear to be established.

At the time these experiments on demethylation were performed (1916), we were unable to find any record of similar work on this subject, apart from the well-known phenomenon of the transfer at above 300° of alkyl groups from nitrogen to the ring.

According to Schultz ("Chemie des Steinkohlentheers," 1900, 3rd ed., I, p. 98), monoethylaniline may be prepared by heating aniline hydrochloride with diethylaniline. No yields or references to the original literature are given, but the reaction is obviously not quantitative, since it is stated that the hydrochloride of diethylaniline remains in solution.

#### EXPERIMENTAL.

*Preparation of Monomethylaniline according to D.R.-P. 75854.*

*Materials Used.*—One hundred grams of aniline, 80.5 grams of formaldehyde (37 per cent.), 30 grams of methyl alcohol, 25 grams of sodium hydroxide solution (D 1.38), 150 grams of zinc dust, 1 litre of water, and 225 grams of sodium hydroxide solution.

\* The published statements concerning the yields of monomethylaniline obtained in this way are very contradictory. See Wahl-Atack, "Organic Dyestuffs," p. 70; Cain, "Intermediate Products," p. 61; Lunge, "Chem. Techn. Untersuchungsmethoden," Vol. III, p. 761; Friedländer, "Fortschritte der Teerfarbenfabrikation," 1877–1887, p. 6.

The first four ingredients were mixed in a wide-mouthed bottle fitted with a stirrer and a reflux condenser, the zinc dust and water then added, and the temperature raised to about  $90^{\circ}$ . The remainder of the sodium hydroxide solution was gradually introduced and the stirring continued at this temperature until, after about twelve to fifteen hours, the methyleneaniline had disappeared. The bases were then distilled in a current of steam, extracted with ether, and a portion converted into the nitrosoamine. Yield of bases, 102 grams. Theory = 115 grams.

Thirty grams of the mixture gave 23 grams of dry phenylmethyl-nitrosoamine, whence the total yield of monomethylaniline is 54.5 per cent. of the theoretical.

*Preparation of Monomethylaniline according to French Patent 212506.*

In these experiments, the quantities of material and method of procedure were as described above, with the exception that the whole of the sodium hydroxide solution was added at once.

In one case, where particularly efficient stirring was employed, the methyleneaniline had disappeared in six and a-half hours. In this experiment, the mixed bases contained 65 per cent. of monomethylaniline (by the nitrosoamine method of analysis), corresponding with a yield of 51.5 per cent. Other experiments with the same quantities and under similar conditions gave yields of 41.5 and 53.5 per cent. of the theoretical quantity of monomethylaniline.

*Reduction in the Presence of Excess of Formaldehyde.*

In two experiments on 100 grams of aniline, in which 0.5 molecular proportion of formaldehyde was used in excess, the yields of monomethylaniline were 46.5 and 55 per cent. In the first case, about 17 grams of the hydrochloride of *p*-nitrosodimethylaniline were obtained on nitrosification.

With an excess of 9 molecular proportions of formaldehyde, two experiments according to the German Patent gave scarcely any monomethylaniline; the reactions proceeded very slowly, and in one case much dimethylaniline was produced.

*Reduction in Concentrated Alcoholic Solution.*

One hundred grams of aniline, 25 grams of formaldehyde (36 per cent.), 840 grams of alcohol, 88 grams of solid sodium hydr-

oxide, 25 grams of aqueous sodium hydroxide (D 1.38), and 150 grams of zinc dust were vigorously stirred together. The reaction was complete in seven and a-half hours at about 60°, and the yield of methylaniline was 46.5 per cent. of the theoretical.

*Reduction of s-Diphenylmethylenediamine.*

Thirty grams of *s*-diphenylmethylenediamine, 125 grams of sodium hydroxide solution (D 1.38), 75 grams of zinc dust, 500 c.c. of water, and 25 grams of alcohol were mixed and vigorously stirred for ten and a-half hours at 70–90°. When a portion dissolved to a clear solution in dilute acetic acid (in which *s*-diphenylmethylenediamine is but sparingly soluble), the products were distilled in a current of steam.

Twenty-two grams of mixed bases were obtained, which gave 13 grams of phenylmethylnitrosoamine, corresponding with a yield of 10.2 grams of monomethylaniline. From the diazonium chloride solution, 10 grams of phenol were isolated, corresponding with 10 grams of aniline.

*Reduction of the Condensation Product of Formaldehyde and Monomethylaniline.*

Fifty grams of monomethylaniline, 19 grams of formaldehyde (36 per cent.), and 5–10 c.c. of aqueous sodium hydroxide were mixed, well shaken, and allowed to remain overnight.

The condensation product was separated by extraction with ether and reduced with a mixture of 150 grams of zinc dust, 1000 c.c. of water, 60 grams of methyl alcohol, and excess of sodium hydroxide solution at about 80°. After one and a-half days, the bases (44 grams) were removed by steam distillation. Nitrosification showed the product to contain 35 grams of monomethylaniline, whilst 9 grams of *p*-nitrosodimethylaniline hydrochloride were obtained.

*The Interaction of Aniline Hydrochloride and Methyl Alcohol in an Autoclave and in Sealed Tubes.*

In these experiments, the methylaniline was determined as the nitrosoamine and the aniline as phenol after decomposition of the diazonium salt. Dimethylaniline was separated and weighed as *p*-nitrosodimethylaniline hydrochloride, but as some of this always remained in solution, the figures for the tertiary base are low.

In experiment 8, aniline (140 grams) and sulphuric acid (16 grams) were used instead of aniline hydrochloride. Experiments 9-13 were made in sealed tubes, and in Nos. 11, 12, and 13 acetic acid (12 grams) was added.

Experi- ment.	Aniline hydro- chloride.	Methyl alcohol.	Tempera- ture.	Time in hours.	Percentage yield		
					Aniline.	Methyl- aniline.	Dimethyl- aniline.
1	110	32	180°	2½	—	48.0	—
2	110	32	180	2½	27.0	51.5	—
3	110	32	180	2½	25.5	53.0	16.5
4	220	64	180	2½	36.0	52.0	7.0
5	220	64	190	5½	34.0	55.0	7.0
			above				
6	220	64	180	4½	26.0	53.0	10.0
7	220	96	180	3	—	45.0	20.0
8	140	84	190	4½	32.0	40.5	16.0
9	22	6.4	180	3	19.0	58.0	11.0
10	22	7.0	175	6	13.0	54.0	13.0
11	22	6.4	170	5	—	56.0	—
12	22	6.4	225	3	—	41.0	—
13	22	6.4	220	3	—	47.5	—

#### *Methylation of Aniline under other Conditions.*

(1) Twenty-six grams of aniline hydrochloride, 7 grams of methyl alcohol, and 25 c.c. of hydrochloric acid were heated in a sealed tube for six hours at 200—210°. Nitrosoamine=13.5 grams; yield of methylaniline=49.5 per cent.

(2) Thirty-six grams of aniline zincchloride and 6.4 grams of methyl alcohol were heated in a sealed tube for seven hours at 180°. Nitrosoamine=7.5 grams; yield of methylaniline=28 per cent.

(3) Twenty-two grams of aniline hydrochloride, 6.4 grams of methyl alcohol, and 15 grams of anhydrous calcium chloride were heated at 160° for three hours. Nitrosoamine=10 grams; yield of methylaniline=43 per cent.

(4 and 5). Twenty-eight grams of aniline (in the presence of 0.2 gram of iodine) were heated in one case with 10 grams, in another with 6.5 grams, of methyl alcohol for nine hours at about 220° (Knoll and Co., D.R.-P. 250236). In both cases, nitrosoamine=15 grams. Yield of methylaniline=42 per cent.

#### *The Demethylation of Dimethylaniline.*

*First Series.*—Interaction between aniline hydrochloride (13.0 grams) and dimethylaniline (12.0 grams) in molecular proportions in sealed tubes.



204 THE PREPARATION OF MONOMETHYLANILINE.

Experiment.	Temperature.	Time in hours.	Nitroso-amine.	Percentage yield of monomethylaniline
1	180°	6	12.5	46
2	200	6	15.0	55
3	230—235	5½	15.0	55

*Second Series.*—Interaction between dimethylaniline hydrochloride (31.5 grams) and aniline (18.6 grams) in molecular proportions in sealed tubes.\*

Experiment.	Temperature.	Time in hours.	Nitroso-amine.	Percentage yield of monomethylaniline
1	180°	3	4	14.5
2	180	6	11.5	21.0
3 <sup>1</sup>	200	13	28.0	51.0

<sup>1</sup> In Experiment 3 about 5 grams of a white solid separated on diluting the contents of the tube. This melted indefinitely at 144°, and after crystallisation from light petroleum indefinitely at about 160°. It was only superficially examined, and appeared to be a tertiary halogen-free base, possibly containing methyl groups in the benzene nucleus.

When 12 grams of dimethylaniline and 9.5 grams of aniline (molecular proportions) were heated for three hours at 220°, practically no monomethylaniline was produced.

Demethylation was found to occur when the two hydrochlorides were heated for three hours at 180°; thus, 13 grams of aniline hydrochloride and 15.8 grams of dimethylaniline hydrochloride (molecular proportions) gave 5.5 grams of the nitrosoamine, corresponding with a 20 per cent. yield of monomethylaniline.

*The Separation of Aniline and Monomethylaniline\* using Zinc Chloride.*

A mixture of aniline and monomethylaniline was treated with an aqueous solution of anhydrous zinc chloride. The precipitate was collected and thoroughly washed with light petroleum. After evaporation of the solvent, the residue of crude methylaniline was weighed and converted into the nitroso-derivative, which was removed from the mixture by extracting three times with ether, dried, and weighed.

The acid liquid which remained after the removal of the nitrosoamine, and contained traces of benzenediazonium chloride, was heated, saturated with salt, the phenol extracted with ether, and finally weighed. The aqueous filtrate from the zincchloride precipitate contained practically no aniline or methylaniline hydrochlorides.

\* In Experiment 1 half these quantities were employed.

The accuracy of this method was checked by regeneration of the aniline from a given weight of the zincichloride

*Analytical Results.*—*Taken:* Aniline 20 grams, methylaniline 20 grams, fused zinc chloride 22 grams, water 50 c.c.

*Obtained:* Zincichloride, 37 grams, whence aniline = 19.2 grams. Phenylmethylnitrosoamine, 23.7 grams, whence methylaniline = 18.7 grams. Phenol, 0.25 gram, whence aniline = 0.25 gram.

There was also obtained 0.5 gram of bases from the aqueous filtrate from the zincichloride.

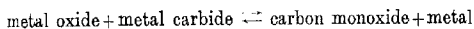
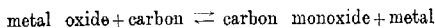
THE UNIVERSITY,  
BIRMINGHAM.

[Received, February 6th, 1919.]

#### XXIV.—*Equilibria in the Reduction of Oxides by Carbon.*

By ROLAND EDGAR SLADE and GEOFFREY ISHERWOOD HIGSON.

Equilibria of some reactions of the type:



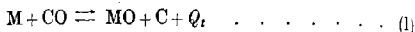
have been investigated.

In either of the above systems there are three components, namely, metal, carbon, and oxygen, and four phases, namely, metal, metal oxide, carbon (or carbide), and carbon monoxide (gas). The number of degrees of freedom is thus  $3 + 2 - 4 = 1$ . Therefore at one temperature there is one pressure of carbon monoxide which determines the equilibrium of the system.

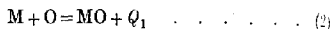
The following experimental method was adopted. A small quantity of the metal was heated in a vacuum to a certain temperature, and carbon monoxide was then admitted until the pressure was greater than the equilibrium pressure. The reaction proceeded in the direction from right to left, and carbon monoxide was absorbed until the equilibrium pressure was attained. Some carbon monoxide was then removed, when the reaction proceeded from left to right until the equilibrium pressure was again attained. If the carbon formed in the first part of the experiment did not remain as a separate phase either as a carbon or as a carbide, but formed a solid solution with the metal, there would be only two solid phases present with the gas phase; the system would there-

fore have two degrees of freedom, and the pressure of carbon monoxide would depend on the relative amounts of metal and carbon present, as well as on the temperature. When the equilibrium was attained from left to right, there was less carbon monoxide present than when the equilibrium was attained from right to left, therefore the equilibrium pressures would have been different in these two cases if there were only two solid phases present.

The equilibrium may be calculated from the heat of reaction by making use of the Nernst heat theorem. In the reaction



where M is the weight in grams of any metal combining with 16 grams of oxygen, and  $Q_i$  is the heat of reaction; in all cases  $Q_i$  is positive, so that increase in temperature will cause the formation of M + CO. That is to say,  $p_{CO}$  increases with the temperature. This quantity of heat,  $Q_i$ , may be considered as the differences of two quantities of heat,  $Q_1$  and  $Q_2$ , for if we write



then, on addition,  $M + CO = MO + C + (Q_1 + Q_2)$ .  $Q_2$ , the heat of dissociation of carbon monoxide, is -29,000 calories, therefore

$$Q_i = Q_1 - 29,000 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Neglecting terms containing  $T^2$ , the Nernst heat theorem requires that

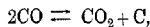
$$\log p_{CO} = \frac{-Q_0}{4.571 T} + 1.75 \log T + 2.6 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where  $Q_0$  is the heat of reaction at absolute zero.

The thermodynamic constant used for carbon monoxide is the value given by Weigert in Abegg's "Handbuch." The relation between  $Q_0$  and  $Q_i$  is given by the equation

$$Q_0 = Q_i + 3.5T \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

*Limits of the Investigation.*—The equilibrium mentioned above could only be determined at temperatures at which the equilibrium,



is practically completely in the left-hand direction. Rhead and Wheeler (T., 1910, 97, 2187; 1911, 99, 1140) have investigated this equilibrium, and from their results it is possible to calculate the partial pressure of carbon dioxide in equilibrium with carbon monoxide at 760 mm. or 50 mm. These values are given in table I.

TABLE I.

Temperature.	Pressure of carbon dioxide in mm. when pressure of carbon monoxide is 760 mm.	Pressure of carbon dioxide in mm. when pressure of carbon monoxide is 50 mm.
850°	53.8	0.23
900	17.6	0.076
1000	4.6	0.0020
1100	0.90	0.00082
1200	0.46	0.00020

From these figures, it is seen that if the equilibrium pressure is as low as 50 mm., there is no complication due to the presence of carbon dioxide at temperatures from 850° upwards. If, however, the pressure is as great as 760 mm., the amount of carbon dioxide present is appreciable up to 1200°. If a carbide is present instead of free carbon, the ratio of carbon dioxide to carbon monoxide will be greater, for we have

$$\frac{p_{\text{co}}^2}{p_{\text{co}_2} p_{\text{c}}} = K,$$

and  $p_{\text{c}}$  (partial pressure of carbon vapour) will be lower over a carbide than over carbon.

In all our experiments, the equilibrium pressures were sufficiently low and the temperature was sufficiently high for the pressure of carbon dioxide to be negligible.

The metals with which we could determine the above equilibrium were only such as would fulfil the following conditions: (1) The metals must not be volatile at the temperature of the experiments. At these temperatures, the vapour pressure of the metal should certainly not be more than 0.25 mm., or it will distil rapidly on to parts of the platinum tube which are at a somewhat lower temperature, and probably attack the platinum. Platinum tubes were, in fact, destroyed by the volatility of boron and manganese. (2) The equilibrium pressure must not be greater than 50 mm. at 850°, or the quantity of carbon monoxide in the gas phase will be appreciable. (3) The equilibrium pressure must be sufficiently great to be measurable. It must be at least 1 mm. at 1300°. Applying the Nernst heat theorem to the equilibrium, we should only expect those elements of which the heat of oxidation, per gram-atom of oxygen, lies between 75,000 and 114,000 calories, to give an equilibrium pressure measurable in our apparatus. Of substances with known heats of oxidation, only silicon, boron, and manganese lie within this range. The only likely metals for which

the heats of oxidation were unknown, and which were readily obtainable, were vanadium, tantalum, and chromium.

*Apparatus.*—The furnace, which has been described by Slade (*Proc. Roy. Soc.*, 1912, [A], 87, 519), consists of a platinum tube 2 cm. in diameter heated by a current of 300 to 400 amperes at 2 to 4 volts. The furnace is placed in a vessel which can be exhausted to prevent the platinum tube from collapsing under the pressure of the atmosphere. A silver capillary tube is used to connect the furnace with the glass tube leading to the pressure gauge. The temperatures were determined by means of a platinum-platinum (90 per cent.)–rhodium (10 per cent.) thermocouple. The couple was calibrated up to the melting point of copper, 1083°, and higher temperatures were determined by extrapolating by means of the formula

$$\log e = 1.22 \log t - 2.65,$$

where  $t$  is expressed in degrees centigrade and  $e$  in millivolts. The cold end of the couple was kept at 0°.

It was found to be impossible to use a platinum boat for any of the substances investigated, for although the temperatures were well below their melting points, they were rapidly alloyed with platinum. Accordingly, boats of unglazed Royal Berlin porcelain were employed.

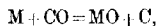
Pressures were read on a mercury vacuum manometer, behind which was a glass millimetre scale illuminated by a lamp and a milk-glass screen. The readings were made with a telescope, and were accurate to  $\pm 0.05$  mm.

The carbon monoxide was prepared by running pure formic acid into concentrated sulphuric acid at 70–80°. The gas, which was first passed through a long tube of soda-lime and then through a similar tube of phosphoric oxide, was collected and stored over mercury in a vessel of 1 litre capacity.

The gas was led from the reservoir to the furnace and pressure gauge by means of a tube, in which were placed two taps separated by a capillary tube of such dimensions that the volume between the two taps was 0.2 c.c. By filling this tube with carbon monoxide at the ordinary temperature, then closing one tap and opening the other, 0.2 c.c. of carbon monoxide was allowed to flow into the exhausted furnace and the tubes connecting the furnace to the gauge and pump. The total volume of this part of the apparatus was about 50 c.c., and when the furnace was heated to about 1200°, its effective volume was about 30 c.c., so that the introduction of 0.2 c.c. under a pressure of one atmosphere caused a rise of pressure of  $\frac{0.2}{30}$  atmosphere, or about 5 mm. of mercury.

In most of the experiments, 0.1 gram of the metal under investigation was introduced into the boat. That this was sufficient may be seen from the following considerations.

If the reaction is



where M is two equivalents of an element, then two gram-equivalents of the element would react with 22,400 c.c. of carbon monoxide. If the pressure in the furnace was 60 mm., which was the maximum pressure used in several cases, the volume of gas contained in the furnace was 2.4 c.c. when measured at N.T.P., therefore to absorb all this gas,  $\frac{2.4}{22,400} \times 2 = 2.2 \times 10^{-4}$  gram-equivalent

of the element would be required. If the equivalent were as great as 100, only 0.02 gram would be required. The metal was usually broken into small pieces, as the velocity of the action must be proportional to the surface exposed.

*Experiments with Vanadium.*—As vanadium is a very refractory substance and is difficultly reducible (that is, the oxide has a high heat of formation), it was decided to attempt to measure the reduction equilibrium.

Some preliminary experiments were made on the action of vanadium on platinum and the melting point of vanadium. The vanadium was placed, in very small pieces (about 0.5 mm. in diameter and less), on a platinum strip which was heated in an atmosphere of hydrogen by an electric current. At 1400°, the vanadium adhered to the strip when the heating had been carried on for some three minutes. The temperature was determined by means of a Wanner pyrometer, correction being made for black-body radiation of the platinum. In another experiment, the strip was dusted with powdered vanadium and heated rapidly until it fused at one point. Examination under the microscope showed that the vanadium had then fused into globules just round the portion of the strip which had fused. The melting point of this vanadium is therefore just below the melting point of platinum, namely, 1760°. The vanadium had been prepared in the electric furnace, and contained 4.6 per cent. of carbon. The carbon probably exists as the carbide, VC, and may be present in solid solution, although the fact that so much carbon is present makes it seem probable that the carbide exists as a separate phase.

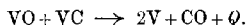
*Experiments.*—0.0636 Gram of the metal was placed in an unglazed porcelain boat in the platinum tube furnace. The furnace was exhausted and left for sixteen hours, when no rise of pressure was noticeable. The temperature was raised to 1000°, and the occluded gas from the boat pumped off; 0.2 c.c. of carbon mon-

oxide was then admitted, and this raised the pressure to 6 mm., at which it remained. Therefore the equilibrium pressure was greater than this, or the velocity of reaction at this temperature was very small. The latter was found to be the case, for when the pressure of carbon monoxide had been increased to 60 mm., there was still no reaction. The temperature was then raised to 1340°, and maintained at this temperature for four and a-half hours. During this time, the pressure fell at first rapidly, and finally became steady at 1.7 mm. The temperature was then reduced to 1145°, where it was maintained for thirty minutes. The pressure fell rapidly to 0.55 mm., where it remained constant. The temperature was then lowered to 900°, when the pressure fell only to 0.2 mm.

On the following day, the furnace was heated to 1340° and the temperature kept constant. In one hour the pressure rose to 1.2 mm., at which it remained constant for three and a-half hours.

The equilibrium pressure at 1340° was therefore between 1.7 and 1.2 mm. The mean of these values is 1.45 mm. At lower temperatures, the equilibrium was attained too slowly to be determined.

The reaction is probably



The value

$$p_{\text{CO}} = \frac{1.45}{760} \text{ atm. at } 1340^\circ$$

gives, by the Nernst heat theorem, the value

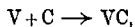
$$Q_0 = 80,875 \text{ cal.}$$

Substituting this in equation (5), we find that

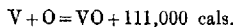
$$p_{\text{CO}} = 1 \text{ atmosphere at } 1827^\circ.$$

This is the temperature at which vanadium oxide would be reduced by the carbide under a pressure of one atmosphere.

There is no direct evidence as to the heat of formation of vanadium carbide, that is, of the reaction



but usually the heats of formation of carbides are small (Wartenberg, *Zeitsch. anorg. Chem.*, 1907, **52**, 299), that is to say, not greater than 2000—3000 calories per gram-atom of carbon. If this heat of formation of the carbide is neglected, an approximate value of the heat of oxidation of vanadium at 20° can be obtained:



Not much trust can be placed in this value, however, for the carbide may be in solid solution in the metal and not as a separate phase.

*Experiments with Tantalum.*—The tantalum used was a portion of a specimen obtained from the late Dr. Werner von Bolton, and used by von Hevesy and Slade to determine the electrode potential of tantalum. It was in the form of a rolled sheet about 0.25 mm. thick. As only a small quantity of the metal was available, 0.035 gram was used in each experiment. If the tantalum was oxidised to the oxide,  $Ta_2O_5$ , this metal would absorb 3.5 c.c. of carbon monoxide. In the first experiment with tantalum, the metal was in the form of one piece of sheet. At  $1000^\circ$ , 2 c.c. of carbon monoxide were admitted ( $p=60$  mm.); the pressure fell, and in two hours became constant at 0.7 mm. The temperature was then raised to  $1200^\circ$  and 0.6 c.c. of carbon monoxide was admitted, so that the pressure was raised to 14 mm. As the pressure did not fall, more carbon monoxide was admitted until the pressure was 40 mm., but there was still no action. The furnace was therefore exhausted, but no appreciable rise in pressure took place in two hours. It therefore seemed probable that the constant pressure of 0.7 mm. obtained at  $1000^\circ$  was not a true equilibrium pressure, but that the equilibrium pressure, even at  $1200^\circ$ , was very low indeed.

In the next experiment the same quantity of metal was used, but it was cut into as many strips as possible, in order to increase the surface. After pumping out all gases from the boat at  $1150^\circ$ , 0.4 c.c. of carbon monoxide was admitted, so as to raise the pressure to about 13 mm. In half an hour the pressure fell to 0.2 mm., and then became constant, and remained so for half an hour. An attempt was now made to reach the equilibrium from the low pressure side. The furnace was exhausted and the temperature was raised to  $1270^\circ$ . In four hours the pressure rose slightly above 0.1 mm. (perhaps 0.12 mm.), and remained constant for about three hours. Carbon monoxide (about 0.1 c.c.) was then admitted to raise the pressure to 2.5 mm., and in one hour the pressure fell to 0.1 mm. This value is therefore the equilibrium pressure at  $1270^\circ$ .

It was impossible to determine the equilibrium at a higher temperature, because at this stage of the work the platinum tube had become weakened and slowly collapsed when kept exhausted for several hours at  $1270^\circ$ , although the external pressure on the tube was only 30–40 mm. of mercury.

*Experiments with Chromium.*—The temperature of reduction of chromium sesquioxide was determined by Greenwood (T., 1908, **93**, 1438), who found that this oxide was reduced at  $1195^\circ$  under a



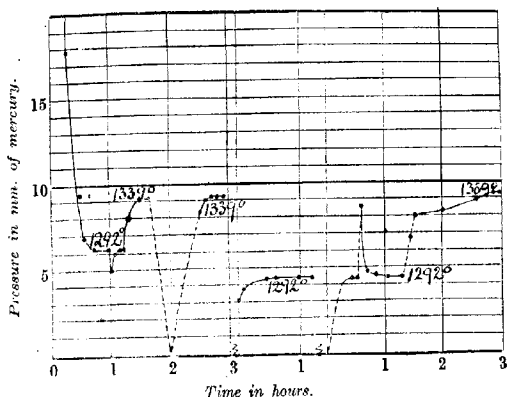
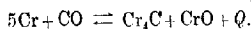
pressure of 2 mm. The boiling point of chromium is  $2200^{\circ}$  (Greenwood), and from this value the vapour pressure of liquid chromium can be calculated to be 0.07 mm. at  $1000^{\circ}$ , 0.078 mm. at  $1100^{\circ}$ , 0.7 mm. at  $1200^{\circ}$ , and 1.12 mm. at  $1300^{\circ}$ . It was therefore not safe to heat chromium to a much higher temperature than  $1200^{\circ}$  in the platinum furnace.

The chromium had been prepared by the Goldschmidt method, and therefore contained a trace of aluminium. As aluminium is easily and completely oxidised by carbon monoxide, it is probable that it would only have a very slight influence on the equilibrium.

0.45 Gram of metal, in the form of a coarse powder, was used in the first experiment. The furnace was heated to  $936^{\circ}$ , and all adsorbed gases were pumped out. Carbon monoxide was then admitted until the pressure was 100 mm. In nine and a-half hours the pressure fell to 22 mm., but did not appear to be approaching a steady value. After remaining for eighty-five hours, the furnace was heated to  $1010^{\circ}$  and carbon monoxide admitted until the pressure was 50 mm. In six hours the pressure fell to 0.75 mm., and appeared to be constant. After eighteen hours, the temperature was raised to  $1292^{\circ}$ , and carbon monoxide admitted until the pressure was 63 mm. In forty-five minutes the pressure fell to 6.2 mm., and remained constant. Carbon monoxide was then pumped out until the pressure fell to 5 mm. In fifteen minutes the pressure rose to 6.2 mm., and remained constant. The temperature was then raised to  $1339^{\circ}$ , and in twenty-five minutes the pressure had risen to 9.1 mm., and become constant. The furnace was then cooled, and next day was heated to  $1339^{\circ}$ . In twenty minutes the pressure rose to 9.2 mm. The furnace was now cooled to  $1292^{\circ}$ , and carbon monoxide was pumped off until the pressure was less than 1 mm. In an hour the pressure became constant at 4.4 mm. The furnace was cooled, and the next day was heated to  $1292^{\circ}$ ; the pressure rose to 4.4 mm. Carbon monoxide was then admitted until the pressure was 8.6 mm. In forty-five minutes the pressure fell to 4.4 mm. The temperature was now raised to  $1339^{\circ}$ , when the pressure rose to 9.2 mm. In the figure are given some of the time-pressure curves obtained. These show how accurately the results could be reproduced.

A new sample of chromium (0.45 gram) was now introduced into the furnace, and the temperature was raised to  $1292^{\circ}$ , carbon monoxide being admitted until the pressure was 15 mm. In twenty minutes the pressure fell to 6.2 mm., and remained constant at this value for one hour. The temperature was then raised to  $1339^{\circ}$ , and the pressure rose to 9.1 mm., but the platinum tube began to leak, owing to its being attacked by the chromium, which had distilled on to it during this and former experiments.

Table II shows the values for the equilibrium pressure obtained with chromium. All these equilibrium pressures were obtained twice from each side. The high value at 1292° is the value obtained when the furnace had not been raised to a higher temperature. After the temperature had been raised to 1339° and lowered again to 1292°, the equilibrium pressure was 4.4 mm., and this value could be obtained again and again. Since chromium easily forms a carbide, it is probable that the reaction taking place was



Calculating the heat of reaction per gram-atom of oxygen at 1315° from the Nernst formula and the van't Hoff formula, the values given in table II are obtained.

TABLE II.

Temperature.	Pressure of carbon monoxide in mm.	$Q_i$ calculated, Nernst.	$Q_i$ calculated, van't Hoff.
1292°	6.2	73,600	—
1339	9.2	69,200	77,000
1292	4.4	69,200	

The value 77,000 calories is the heat of reaction calculated from the integrated form of the van't Hoff equation,

$$Q_i = -4571 (\log p_2 - \log p_1) \frac{T_1 T_2}{T_2 - T_1}.$$

In this method of calculating  $Q_i$ , an error of 0.1 mm. in the determination of the equilibrium at 1292° would make a difference of a little more than 1000 calories in the value of  $Q_i$ . The assumption on which this formula is based, however, is only that the heat

of reaction does not change appreciably between the two temperatures. That two different values were obtained for the equilibrium at 1292°, according to whether the furnace had been heated up to 1339° or not, must be explained by supposing that the substances in equilibrium were different in the two cases. It is very improbable that the first value is due to the presence of a trace of aluminium in the metal, for the presence of aluminium would be expected to lower rather than to raise the equilibrium pressure, and in the two experiments in which the pressure was 6.2 mm., very different amounts of carbon monoxide had been absorbed by the same amount of metal. In the first experiment, 6–7 c.c. of carbon monoxide, and in the second case only 0.6 c.c., were absorbed.

The equilibrium in the gas phase is represented by

$$p_{\text{CO}} = K \cdot \frac{p_{\text{carbide}}}{p_{\text{metal}}} \cdot \frac{p_{\text{oxide}}}{p_{\text{metal}}}$$

The change in the system caused by raising the temperature to 1339° was to give a lower equilibrium pressure at 1292°, and this must be due to (1) increase in the partial pressure of chromium, (2) lowering of the partial pressure of the carbide, or (3) lowering of the partial pressure of the oxide.

Case (1) might be caused by the existence of a transition point of chromium between 1292° and 1339°. At first, the metal is in the  $\alpha$ -form, stable at lower temperatures; on heating, the metal would change to the other, or  $\beta$ -form, and on cooling to 1292° would not revert to the  $\alpha$ -form, but remain in the unstable  $\beta$ -form, which would have a higher vapour pressure than the  $\alpha$ -form.

Case (2) might be caused by the formation of an unstable carbide in the first instance, which on heating to 1339° changes into the stable form. On cooling now to the lower temperature, the unstable carbide is not formed in the presence of the more stable one.

Case (3) might be caused by the chromium oxide combining with the silica in the boat to form a silicate, but this reaction should not be different after the furnace had been raised to the higher temperature. The first explanation seems the more probable.

This investigation was carried out in the Muspratt Laboratory of Physical Chemistry, University of Liverpool.

BRITISH PHOTOGRAPHIC RESEARCH ASSOCIATION LABORATORY.

[Received, February 14th, 1919.]

# PROCEEDINGS

## OF THE

# CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, June 5th, 1919, at 8 p.m., Sir JAMES J. DOBBIE, D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society through the death of the following Fellows:

	<i>Elected.</i>	<i>Died.</i>
Thomas Fairley .....	May 15th, 1865.	Feb. 21st.
James Baird MacLachlan .....	May 4th, 1916.	May 25th.
Sir Boverton Redwood, Bart. ....	Jan. 18th, 1866.	June 4th.

Messrs. S. J. Hopkins, G. A. R. Kon, F. T. Stevenson, N. Singer, and H. G. Tribley were formally admitted as Fellows of the Chemical Society.

Certificates for election were read for the first time in favour of:

William Barnes, 29, Conway Road, Luton.  
 Frank Leslie Barrett, 46, Grantham Road, Horton, Bradford.  
 Harold Ward Dudley, 10, Lanark Mansions, Maida Vale, W.9.  
 Herbert William Gorbald, 45, Falmouth Avenue, Highams Park, E.4.  
 Sampson Manson Hing, Y.M.C.A., Tottenham Court Road, W.1.  
 Clive Newcomb, B.A., M.B., B.Ch., 48, Leigham Court Road, Streatham, S.W.16.  
 Isaac Sklar, 29, Clark Street, Stepney, E.1.  
 Colin Everett Spearing, Winslade, Eversfield Road, Reigate.  
 Ernest Edward Wallen, 8, Glade Street, Bolton.  
 Arthur Charles Vincent Weston, 24, Belsize Park Gardens, Hampstead, N.W.3.  
 Harold Bishop Williams, 6, Hamlet Road, Upper Norwood, S.E.19.

The following papers were read:

- "An isotonic (isosmotic) apparatus for comparing molecular weights. Part I." By P. BLACKMAN.
- "The 'active substance' in the iodination of phenols." By V. COFMAN.
- "The chemistry of the glutaconic acids. Part XI. The occurrence of 1:3-addition to the normal form." By J. F. THORPE.
- "The formation and reactions of imino-compounds. Part XIX. The chemistry of the cyanoacetamide and Guareschi condensations." By G. A. R. KON and J. F. THORPE.

Ordinary Scientific Meeting, Thursday, June 19th, 1919, at 8 p.m., Sir JAMES J. DOBBIE, D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of the following Fellows:

	<i>Elected.</i>	<i>Died.</i>
Samuel Godfrey Hall .....	Feb. 18th, 1899.	June 9th.
Walter Parker .....	Feb. 5th, 1917.	April 15th.
James Fleming Stark .....	Dec. 15th, 1870.	June 13th.

It was announced that a communication had been received from the Committee of the Van't Hoff Fund for the endowment of research in pure and applied chemistry. The amount from this fund available for distribution during 1920 is about £140.

A Committee, consisting of Professor A. F. Holleman (President), Professor S. Hoogewerff, Professor A. Smits, and Professor E. H. Büchner (Secretary), has been appointed to award grants. Applications should be sent before November 1st, 1919, by registered post, to "Het Bestuur der Koninklijke Akademie van Wetenschappen: bestemd voor de Commissie van het 'Van't Hoff-fonds' Trippenhuis, Kloveniersburgwal, te Amsterdam." Every applicant is requested to submit a detailed account of the manner in which he proposes to expend the grant and to state the reasons for which he makes his application.

Papers embodying the results of the research may be published in any journal, but acknowledgment must be made of the source of the grant. Copies of papers containing the results of the research must be forwarded to the Committee.

Certificates were read for the first time in favour of:

Lawrence Eversley Campbell, B.Sc., 5, St. Matthew's Avenue, Surbiton.  
 Alan Ernest Gardiner, 21, Chestnut Road, W. Norwood, S.E.27.  
 Robert Grant, 24, Edward Street, Woollahua.  
 John Knaggs, B.Sc., South Street, Bridlington.  
 Charles Rose, B.Sc., 803, Chorley New Road, Horwich.

Certificates have been authorised by the Council for presentation to ballot under Bye-law I (3) in favour of:

Douglas Coghill, Kuala Lumpur, F.M.S.  
 Charles Edward Smithraaratchy, B.Sc., Trinity College, Kandy, Ceylon.

Messrs. H. E. Annett and A. J. Chapman were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared duly elected as Fellows:

Donald Bagley.	Denis Madden.
Edgar Beard, B.Sc.	Owen Leonard Maund.
Wilfrid Andrews Bell.	Brian Mead.
Alfred Randolph Campbell.	Rustom Jeejeebhoy Mistri.
Algernon George Crossley.	Charles Jean Stanislas Van Overstraeten.
Ananda Kishore Dás, M.A., B.Sc.	Arthur Pinkerton.
Manik Lal Dey, M.Sc.	Sidney Owen Rawling, B.Sc.
Philip Drinker, B.S.	John David Smith.
John Mouson Errington.	Sidney Albert Lewis Smith.
Archibald Wooster Frame.	Cyril Richard William Stephenson, M.Sc.
John William Gardom.	Arnold Teichfeld.
Robert Stephen Glennie.	Harold Toms.
Cecil Godfrey.	Dudley Cloete Vining.
Sidney Herbert Hadfield.	Edward John Wall.
Harry Harper, B.Sc.	William Wardlaw, M.Sc.
Herbert Hollings Jacques, B.Sc.	Ernest Edward Whale, B.Sc.
Louis Charles Kemp.	David Wingate.
Herbert Joseph Seymour King, B.Sc.	Arthur Samuel Wood, B.Sc.
Cyril Henry Stanley Kipping, M.A.	Thomas Thorne Wood.
Morvan Lapworth, B.Sc.	George Ernest Yarrow, B.Sc.
Alexander Douglas Macallum, B.A.	
Ernest Neil Macallum.	

The meeting was then adjourned and the Informal Meeting declared open.

### THE LIBRARY.

The Library will be closed for Stocktaking from Monday, August 11th, until Saturday, August 23rd, 1919, inclusive.

### LIST OF FELLOWS, 1919.

The List of Fellows for 1919 is now in active preparation, and changes of address received after July 31st cannot be included in it.

In order that the new list may be as complete as possible, those Fellows whose degrees and Christian names do not appear in full are requested to communicate them to the Assistant Secretary.

### ADDITIONS TO THE LIBRARY.

#### I. *Donations.*

ATAK, FREDERICK WILLIAM, and WHINYATES, LEONARD [Editors]. The Chemists' Year Book, 1918—19. 2 vols. London 1919. pp. 1146. 15s. net. (*Reference.*)

From the Publishers: Messrs. Sherratt and Hughes.

FINDLAY, ALEXANDER. Osmotic pressure. 2nd edition. London 1919. pp. xi+116. ill. 6s. net. (*Recd.* 3/6/19.)

From the Publishers: Messrs. Longmans, Green and Co.

RICHARDSON, CLIFFORD. Papers on asphalt and asphalt pavements. (Together with one by E. C. PAILLER on The differentiation of natural and oil asphalt.) 1912—1917. (*Reference.*)

From the Author.

SENDER, GEORGE. Outlines of physical chemistry. 7th edition. London 1919. pp. xx+432. ill. 6s. net. (*Recd.* 13/6/19.)

From the Author.

— A text-book of inorganic chemistry. 5th edition. London 1919. pp. x+621. ill. 7s. 6d. net. (*Recd.* 13/6/19.)

From the Author.

#### II. *By Purchase.*

ABRAHAM, HERBERT. Asphalts and allied substances: their occurrence, modes of production, uses in the arts and methods of

testing. New York 1918. pp. xxv+606. ill. 25s. net. (*Recd.* 27/5/19.)

BEILSTEIN'S HANDBUCH DER ORGANISCHEN CHEMIE. Herausgegeben von der Deutschen Chemischen Gesellschaft, bearbeitet von BERNHARD PRAGER und PAUL JACOBSEN. Vol. I. Acyclische Kohlenwasserstoffe, Oxy- und Oxo-Verbindungen. 4th edition. Berlin 1918. pp. xxxv+983. (Two copies.)

BRACHVOGEL, JOHN K. Industrial alcohol, its manufacture and uses. Based on Dr. Max Maercker's "Introduction to distillation." With special chapters by CHARLES J. THATCHER. New York 1907. pp. xii+516. ill. 18s. net. (*Recd.* 21/5/19.)

LEWES, VIVIAN BYAM. The carbonisation of coal. A scientific review of the formation, composition and destructive distillation of coal for gas, coke and by-products. With an addition on recent developments by ALFRED BROADHEAD SEARLE. London 1918. pp. xiv+287. ill. 12s. 6d. net. (*Recd.* 6/6/19.)

OIL, PAINT AND DRUG REPORTER. Vol. 95, etc. New York 1919+. (*Reference.*)

PARRY, ERNEST JOHN. The chemistry of essential oils and artificial perfumes. Vol. 2. 3rd edition. London 1919. pp. [viii]+344. ill. 17s. 6d. net. (*Recd.* 16/6/19.)

SMITH, G. CARLTON. Trinitrotoluenes and mono- and di-nitrotoluenes: their manufacture and properties. London 1918. pp. vii+133. 8s. 6d. net. (*Recd.* 15/5/19.)

TROTMAN, SAMUEL RUSSELL, and THORP, E. L. The principles of bleaching and finishing of cotton. 2nd edition, revised. London 1918. pp. xii+347. ill. 21s. net. (*Recd.* 14/5/19.)

VAN NOSTRAND'S Chemical Annual. A handbook of useful data for analytical, manufacturing, and investigating chemists, chemical engineers, and students. Fourth issue, 1918. Edited by JOHN C. OLSEN and MAXIMILIAN P. MATTHIAS. London 1918. pp. xviii+778. 15s. net. (*Reference.*)

### III. Pamphlets.

REILLY, JOSEPH. Industrial alcohol. Lecture delivered before the Royal Dublin Society, 19th Feb., 1919. Dublin 1919. pp. 36.

SCIENTIFIC AND INDUSTRIAL RESEARCH, Department of. First report of the Mine Rescue Research Committee. London 1918. pp. 55. ill.

STANSFIELD, ALFRED. The commercial feasibility of the electric smelting of iron ores in B.C. (*Bull. No. 2, Brit. Columbia, Dept. of Mines.*) Victoria 1919. pp. 95.

STEWART, ALAN WEST. The Crismer test for the detection of



foreign fat in butter, lard, &c. (From the *J. State Med.*, 1918, **26**.)

STOPES, MARIE C., and WHEELER, RICHARD VERNON. Monograph on the constitution of coal. (Based on a paper read before the London section of the Society of Chemical Industry.) London 1918. pp. 58. ill.

TILDEN, SIR WILLIAM AUGUSTUS. Books on chemistry. (*Birmingham Reference Library Lectures*.) London [1887]. pp. 55 + ii.

WASHINGTON, HENRY S. Italian leucitic lavas as a source of potash. (From *Met. and Chem. Engineering*, 1918, **18**.)

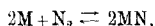
WHITE, ALFRED H., and RUE, JOHN D. Methyl alcohol and acetone as by-products of the soda pulp industry. (From *Paper*, 1917, **19**.)

WILLIAMSON, E. D. The effect of strain on heterogeneous equilibrium. (From the *Physical Rev.*, 1917, **10**.)

XXV.—*The Dissociation Pressures of some Nitrides.*

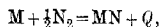
By ROLAND EDGAR SLADE and GEOFFREY ISHERWOOD HIGSON.

Equilibria of the type



where  $M$  is three equivalents of a metal, have been investigated. In this system there are two components, namely, metal and nitrogen, and three phases, namely, metal, nitride, and nitrogen. The number of degrees of freedom is thus  $2 + 2 - 3 = 1$ , and therefore at one temperature there is one pressure of the nitrogen which determines the equilibrium of the dissociation. If the nitride dissolves in the metal as a solid solution, there are only two phases, and the number of the degrees of freedom is therefore two. The equilibrium will then be determined, not only by the pressure of the nitrogen, but also by the composition of the solid phase.

Applying the Nernst heat theorem to the equilibrium



where  $Q$  is the heat evolved when half a gram-molecule of nitrogen combines with the metal, we have

$$\log p_{N_2} = -\frac{Q_0}{4.571T} + 1.75 \log T + 2.6$$

and

$$Q_t = Q_0 - 3.5T,$$

where  $Q_0$  and  $Q_t$ , respectively, are the heats of reaction at absolute zero and some other temperature,  $T$ . As the heats of formation of the nitrides investigated were unknown, it is impossible to apply these equations to determine the value of  $p_{N_2}$ , but it will be seen that the pressure of nitrogen at  $1127^\circ$  would be 1 mm. if the heat of formation of the nitride were 70,600 cal. and 60 mm. if the heat of formation were 59,000 cal.

## EXPERIMENTAL.

The furnace used for the determination of the equilibria is described in the preceding paper.

Nitrogen was prepared by heating a solution containing ammonium chloride, potassium nitrate, and potassium dichromate. The dichromate served to oxidise any oxides of nitrogen to nitric acid, which was absorbed by passing the gas through a long tube of soda-lime. The nitrogen was then dried by passage through a long tube of phosphoric oxide.

The equilibria were determined by heating small quantities of

## 216 THE DISSOCIATION PRESSURES OF SOME NITRIDES.

the metal to a known temperature, introducing nitrogen into the furnace, and determining the value to which the pressure fell. Nitrogen was then pumped out, and the equilibrium was determined from the low-pressure side.

*Vanadium.*—This metal is known to form two nitrides, VN and VN<sub>2</sub>.

At 1203°, the equilibrium pressure was found to be slightly less than 0.2 mm., and at 1271° slightly less than 1.5 mm. The equilibrium pressure is somewhere near these values, but equilibrium was attained very slowly, and it was impossible to heat the platinum tube in use at that time to a higher temperature.

*Boron.*—An attempt was made to determine the dissociation pressure of boron nitride at 1100° and 1240°.

At 1100°, the velocity was too low for the equilibrium to be determined. At 1240°, the pressure of nitrogen fell from 26.4 mm. to 9.4 mm. in six hours, and appeared to be approaching the constant value of about 9 mm., but the boron attacked the platinum tube and caused it to leak, so that further experiments could not be made.

*Tantalum.*—Tantalum is known to form two stable nitrides, TaN and Ta<sub>3</sub>N<sub>5</sub>. In our experiments, it is probable that the lower nitride, TaN, was formed.

When the metal was heated at 1170° in nitrogen under 15 mm. pressure, the gas was slowly absorbed until the pressure fell to 0.5 mm. The furnace was then exhausted to 0.05 mm. The pressure rose in two hours to 0.4 mm.

In another experiment, at 1308°, the pressure fell from 9 mm. to 1.2 mm. in one and a-half hours, and remained constant for half an hour. The furnace was then allowed to cool. Next day it was completely exhausted, and again heated to 1308°. The pressure rose to 0.8 mm., and remained constant at this value for two hours.

### Summary of Results.

	Tempera- ture.	Pressure of nitrogen.	Heat of formation of nitride, that is, $Q_0$ , calculated from Nernst's formula.
Vanadium	1203°	Not greater than 0.2 mm.	79,200 cals.
	1271	" " 1.5	77,200 "
Boron ...	1222	" " 9.4 "	About 69,000 "
Tantalum	1170	0.4—0.5 mm.	74,700—76,500 cals.
	1308	0.8—1.2 "	79,900—82,800 "

This investigation was carried out in the Muspratt Laboratory of Physical Chemistry, University of Liverpool.

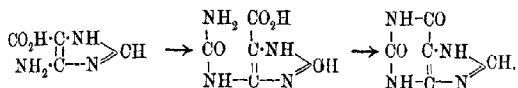
BRITISH PHOTOGRAPHIC RESEARCH ASSOCIATION LABORATORY.

[Received, February 14th, 1919.]

## XXVI.—Nitro-, Arylazo-, and Amino-glyoxalines.

By ROBERT GEORGE FARGHER and FRANK LEE PYMAN.

This investigation was begun with the object of effecting the synthesis of purine derivatives by a method complementary to those which have been employed hitherto. In these, the pyrimidine nucleus is first built up and the glyoxaline ring closed subsequently. We proposed to prepare 4-aminoglyoxaline-5-carboxylic acid,\* condense it with cyanic acid, and eliminate water with the production of xanthine.



Such a synthesis would be of interest in view of the suggestion that purine derivatives originate from histidine in the animal body (compare Hopkins, T., 1916, 109, 629).

Although the starting material for the proposed synthesis, 4-aminoglyoxaline-5-carboxylic acid, was unknown, we did not anticipate that its preparation would offer any serious difficulty. We have, however, so far failed to obtain this substance, and now give an account of our attempts to prepare this and other amino-substituted glyoxalines.

An account of the investigation may be subdivided under three headings: first, the preparation of the glyoxalines and their carboxylic acids, which were required as starting materials; second, the preparation and properties of nitroglyoxalines; and last, the preparation and properties of arylazoglyoxalines.

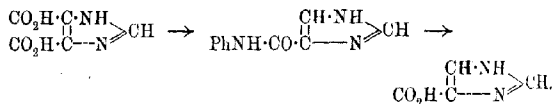
(1) *The Preparation of Glyoxalines and their Carboxylic Acids.*—For the purpose of this investigation, it was necessary to prepare considerable quantities of glyoxaline-4:5-dicarboxylic acid, the most convenient source of glyoxaline. This acid was first prepared by Maquenne (*Ann. chim. phys.*, 1891, [vi], 24, 525), by mixing aqueous solutions of nitrotartaric acid and hexamethylenetetramine, adding ammonia, and allowing the mixture to become hot, and subsequently by Dedichen (*Ber.*, 1906, 39, 1835), who replaced the hexamethylenetetramine by formaldehyde. We have carried out a large number of experiments on the best conditions for the pre-

\* In glyoxalines containing a free imino-group, the 4- and 5-positions are equivalent.

paration of this acid, and find that to obtain a good yield it is essential that the reaction mixture should be kept cold.

A number of experiments were carried out with the object of effecting the partial decarboxylation of glyoxaline-4:5-dicarboxylic acid, and thus producing glyoxaline-4-carboxylic acid by a more convenient and economical process than that previously employed, where six operations are required in its synthesis from citric acid through 4-hydroxymethylglyoxaline (T., 1911, **99**, 668; 1916, **109**, 186). When the acid is heated with water, 10 per cent. hydrochloric acid, or concentrated hydrochloric acid, little decarboxylation takes place below 180°, but above this temperature, the action proceeds more readily, glyoxaline being the main product, whilst a small proportion of glyoxaline-4-carboxylic acid can be isolated provided that the heating has not been too prolonged. When the acid is heated with an excess of concentrated ammonia at 180° to 200°, the main product is glyoxaline,\* and a similar result is obtained by heating the aqueous solution of the mono-sodium salt.

The desired result can be obtained, however, by boiling the acid with aniline, when the *anilide* of glyoxaline-4-carboxylic acid is formed in a yield amounting to 45 per cent. of the theoretical. From this, the acid is readily prepared by hydrolysis.



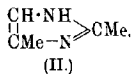
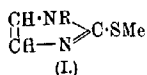
For the purpose of orientation, it was necessary to prepare glyoxalines substituted in the 2-, 4:5-, and 2:4:5-positions. The 2-alkylglyoxalines were prepared by suitable modifications of Maquenne's methods. From 2-methylglyoxaline-4:5-dicarboxylic acid, 2-methylglyoxaline-4-carboxylic acid was obtained through its *anilide*.

As representatives of 4:5- and 2:4:5-substituted glyoxalines, 4:5-dimethylglyoxaline and 2:4:5-trimethylglyoxaline were prepared by modification of known methods.

(2) *Nitroglyoxalines*.—The nitration of various glyoxalines has led to the formation of mononitroglyoxalines in the hands of several observers. In some cases the nitro-group evidently enters the 4- (or 5-) position, since no other position is vacant; for instance, in the nitration of 2-methylthiol-1-phenyl (and 1-methyl) glyoxaline

\* We were unable to find any evidence of the formation of the imide of glyoxaline-4:5-dicarboxylic acid, from which the desired 5-aminoglyoxaline-4-carboxylic acid might have been obtained by the action of hypobromous acid.

(I) (Wohl and Marckwald, *Ber.*, 1888, **22**, 568, 1353) and 2:4-dimethylglyoxaline (II) (Windaus, *Ber.*, 1909, **42**, 758):



The orientation of the nitro-group in nitroglyoxaline itself (Rung and M. Behrend, *Annalen*, 1892, **271**, 28; R. Behrend and Schmitz, *ibid.*, 1893, **277**, 338) and in nitro-4-methylglyoxaline has not been determined previously, but an indication that the latter contains the nitro-group in the 5-position is afforded by Windaus's observation (*loc. cit.*) of its close similarity to 5-nitro-2:4-dimethylglyoxaline.

Moreover, whilst 4-nitro-2-methylglyoxaline is readily prepared, we were unable to obtain a nitro-derivative of 4:5-dimethylglyoxaline, for in this case part of the base was completely oxidised, whilst a considerable proportion remained unchanged, and the only isolable derivative was the nitrate of 4-methylglyoxaline-5-carboxylic acid, which has been described by Gerngross (*Ber.*, 1912, **45**, 509).

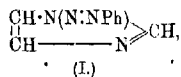
The inability of a glyoxaline substituted in both the 4- and 5-positions to form a nitro-derivative indicates that the nitroglyoxalines contain the substituent in the 4-(or 5-)position. This view is confirmed by their behaviour on reduction. Wohl and Marckwald (*loc. cit.*) attempted to reduce the 4-(or 5-)nitro-2-methylthiol-1-phenyl-(and 1-methyl)glyoxalines to the corresponding amines, but obtained only decomposition products, including methyl mercaptan. Similarly, we find that 4-nitro-2-methylglyoxaline undergoes fission on reduction with tin and hydrochloric acid, two of the three atoms of nitrogen in the molecule appearing in the form of ammonia.\* Since precisely the same result is obtained with nitroglyoxaline and nitro-4-methylglyoxaline, whilst it is shown below that 2-aminoglyoxalines are stable, it is clear that these nitro-derivatives are 4-nitroglyoxaline and 5-nitro-4-methylglyoxaline respectively.

Before we had arrived at this conclusion, we were anxious to prepare some of the nitroglyoxaline-4-carboxylic acid, which Windaus and Opitz (*Ber.*, 1911, **44**, 1721) obtained by the action of boiling 25 per cent. nitric acid on 4-β-hydroxyethylglyoxaline.

\* The first stage in the disintegration of the 4-aminoglyoxalines is probably the elimination of the amino-group as ammonia, with the formation of a glyoxalone, for certain members of the purine group—also derivatives of 4-aminoglyoxaline—have been shown to undergo hydrolysis in this manner (compare, for instance, Tafel and Mayer, *Ber.*, 1908, **41**, 2546; Biltz, *Ber.*, 1910, **43**, 1589).

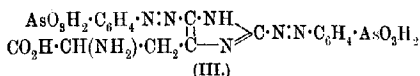
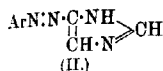
These authors state that the yield of 4- $\beta$ -hydroxyethylglyoxaline, obtained by the action of barium nitrite on 4- $\beta$ -aminoethylglyoxaline hydrochloride, was so poor that the nitro-compound was not available in sufficient quantity for further study. It appeared to us, however, that this nitro-compound might be obtained by the action of nitric acid on other more readily accessible derivatives of glyoxaline containing a side-chain of carbon atoms in the 4-position, and in the first place we employed compounds containing two carbon atoms in the side-chains, like Windaus's starting material. The results were disappointing; 4- $\beta$ -aminoethylglyoxaline, when boiled with 50 per cent. nitric acid for nine hours, was mainly recovered unchanged, whilst 4-cyanomethylglyoxaline was converted under the same conditions almost quantitatively into glyoxaline-4-acetic acid. Attempts to nitrate glyoxaline-4-carboxylic acid and glyoxaline-4:5-dicarboxylic acid were likewise unsuccessful. The prospect of nitrating 4-hydroxymethylglyoxaline was not hopeful, for it has been shown previously (T., 1916, 109, 186) that hot concentrated nitric acid converts it into glyoxaline-4-formaldehyde and glyoxaline-4-carboxylic acid. It has now been found that the alcohol gives the same products when digested on the water-bath with fuming nitric acid, whilst it can be recovered almost quantitatively after boiling with ten parts of 25 per cent. nitric acid for four hours. On the other hand, the nitration of 4-hydroxymethylglyoxaline with nitric and sulphuric acids gave rise to a product which was not obtained in crystalline form, but further study of this was omitted in view of the peculiar behaviour of the simple nitroglyoxalines on reduction.

(3) *Arylazoglyoxalines*.—The constitution of the arylazo-derivatives of simple glyoxalines has not been settled hitherto. Rung and Behrend (*Annalen*, 1892, 271, 28), who first isolated benzeneazoglyoxaline, considered it to be a diazoimino-compound (I), because boiling acids decomposed it with the formation of nitrogen



and glyoxaline. Bräun (*Ber.*, 1904, 37, 696), who prepared many arylazoglyoxalines from diazobenzene-*p*-sulphonic acid and various glyoxalines, adopted the same view of the constitution of these compounds on other grounds, namely, because all the glyoxalines substituted in some or all of the 2-, 4-, and 5-positions which he examined coupled with the diazonium salt, whilst 1-substituted glyoxalines did not. Pauly (*Zeitsch. physiol. Chem.*, 1904, 42, 508), however, pointed out the possibility that the arylazo-

glyoxalines were true *C*-azo-compounds (II) similar to those obtained from pyrrole, and later (*ibid.*, 1915, 94, 284) attributed the probable formula (III) given below to the compound obtained by the action of diazotised arsanilic acid on histidine, owing to its stability towards acids. Whilst in the case of these simple

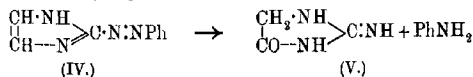


glyoxalines the orientation of the arylazo-group is uncertain, the constitution of the arylazopurines is known, for Hans Fischer (*Zeitsch. physiol. Chem.*, 1909, 60, 69) has shown that the arylazo-group enters the 8-position of the purine nucleus—the 2-position of its glyoxaline ring—by reducing arylazopurines to 8-aminopurines.

In view of this result, it appeared to us probable that the arylazo-derivatives of simple glyoxalines were also *C*-azo-compounds, as Pauly suggested, and it was of interest to determine whether the arylazo-group entered the 2- or the 4-position, and the nature of the products obtained on reduction.

The benzeneazoglyoxaline of Rung and Behrend was first examined. By the method of these workers, it is obtained in poor yield, but by the action of benzenediazonium chloride on one molecular proportion of glyoxaline in an excess of aqueous sodium carbonate, it is readily obtained mixed with a little 2:4:5-*tris*-benzeneazoglyoxaline. 2-Benzeneazoglyoxaline melts at 190° (corr.), and it is therefore evident that the specimen prepared by Rung and Behrend, melting at 177–178°, was impure. The pure substance is reasonably stable towards boiling 10 per cent. hydrochloric acid, for a considerable proportion can be recovered unchanged after two hours.

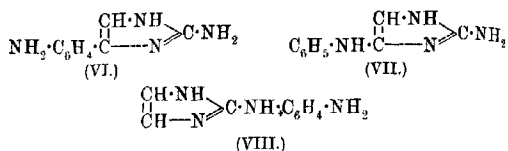
The constitution of 2-benzeneazoglyoxaline (IV) was proved by reduction. With zinc dust and hot acetic acid, it yields aniline and glycoeyamidine\* (V), the formation of the latter showing that the benzeneazo-group is attached to the 2-position of the ring.



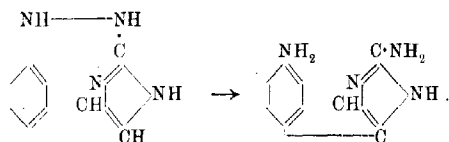
\* The conversion of glyoxaline into glycoeyamidine and 2-aminoglyoxaline, both derivatives of guanidine, is of biochemical interest, firstly, because creatinine is the *N*-methyl derivative of glycoeyamidine, and secondly, on account of the similar behaviour of histidine and arginine in purine metabolism (compare Hopkins, *loc. cit.*).



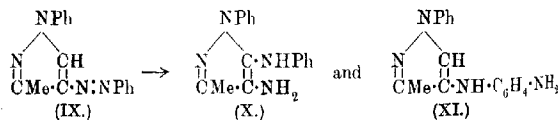
This result is confirmed by the formation of a small amount of guanidine on the reduction of 2-benzeneazoglyoxaline with stannous chloride. In this reduction, a small quantity of 2-aminoglyoxaline is formed and some aniline, but the main product is 2-amino-4-*p*-aminophenylglyoxaline (VI), a compound resulting from a change of the benzidine type. It is also formed in small proportion in the reduction with zinc dust and acetic acid.



Its constitution was proved by the oxidation of its diacetyl derivative with potassium permanganate, when *p*-acetylaminobenzoic acid was formed. This result eliminated the possibility that the compound had one of the two formulæ (VII) or (VIII), representing substances formed by a change of the semidine type. The occurrence of a rearrangement of the benzidine type in a five-membered heterocyclic nucleus seems remarkable at first sight, but a closer inspection of the formula shows that the conjugated system connecting the 2- and 5-carbon atoms of the glyoxaline ring is similar to that existing in the benzene nucleus.



Whilst no other case of the benzidine type of change in a heterocyclic nucleus has been observed previously, so far as we are aware, Michaelis and Schäfer (*Annalen*, 1915, **407**, 229) have obtained by the reduction of 1-phenyl-3-methyl-4-benzeneazopyrazole (IX) the two isomerides (X) and (XI) which result from the two possible changes of the semidine type.

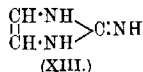
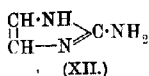


Owing to the formation of 2-amino-4-*p*-aminophenylglyoxaline in the reduction of 2-benzeneazoglyoxaline, the yield of 2-amino-

glyoxaline is small, so for the preparation of this substance the reduction of an arylazoglyoxaline containing a substituent in the para-position of the benzene nucleus was undertaken.

2-*p*-Bromobenzenediazoglyoxaline is the main product of the interaction of *p*-bromobenzenediazonium chloride and glyoxaline in aqueous sodium carbonate, only a very small proportion of 4-*p*-bromobenzenediazoglyoxaline being formed. The reduction of 2-*p*-bromobenzenediazoglyoxaline with stannous chloride gave 2-aminoglyoxaline in a yield of 56 per cent. of the theoretical, together with aniline, guanidine, some 2-amino-4-*p*-aminophenylglyoxaline, and a small quantity of a base,  $C_9H_9N_4Br$ , which is probably 2-5'-bromo-2'-aminoanilino-2-glyoxaline (compare p. 246).

2-Aminoglyoxaline is a monacidic base yielding crystalline salts, but the free base has not been obtained in a crystalline form.



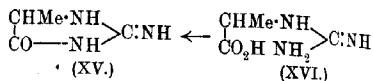
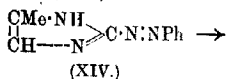
For this compound, the tautomeric formulæ (XII) and (XIII) are possible. The first is supported by the production of a red colour when the substance is mixed with sodium diazobenzene-*p*-sulphonate, and by the fact that, after treatment with nitrous acid, it couples with phenols. An indication that it can also react according to the formula (XIII)—which represents an unsaturated compound no longer containing the glyoxaline ring—is given by its behaviour towards permanganate, for 2-aminoglyoxaline and all the substituted 2-aminoglyoxalines described in this paper reduce cold aqueous acid potassium permanganate, and in this respect resemble the 2-thioglyoxalines (compare T., 1911, 99, 2173), whereas glyoxaline and its homologues are stable to this reagent, although they reduce alkaline permanganate, giving green solutions.

2-Aminoglyoxaline yields a *monoacetyl* and a *monobenzoyl* derivative, which are stable to cold aqueous acid permanganate.

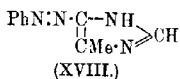
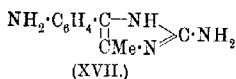
2-Aminoglyoxaline does not combine with benzaldehyde in acetic acid solution. Moreover, 2-amino-5-*p*-aminophenyl-4-methylglyoxaline (XVII) yields only a monobenzylidene compound under these conditions, doubtless 2-amino-5-*p*-benzylideneaminophenyl-4-methylglyoxaline. This behaviour, therefore, serves to differentiate between 2-aminoglyoxalines and homologues of aniline, and is employed later in the determination of constitution.

The action of benzenediazonium chloride on 4-methylglyoxaline proceeded quite differently from its action on glyoxaline. Instead of the 2-substituted arylazo-compound being formed predominantly,

nearly equal quantities of 2-benzeneazo-4-methylglyoxaline, 5-benzeneazo-4-methylglyoxaline, and 2:5-bisbenzeneazo-4-methylglyoxaline were obtained. The constitution of 2-benzeneazo-4-methylglyoxaline (XIV) follows from the fact that it yields, on reduction with zinc dust and acetic acid, alacreatinine (XV), a compound previously synthesised by Baumann (*Annalen*, 1873, 167, 83) by the elimination of water from  $\alpha$ -guanidinopropionic acid (XVI).



This change is precisely similar to the formation of glyco-cyamidine from 2-benzeneazoglyoxaline. 2-Benzeneazo-4-methylglyoxaline behaves in the same way as 2-benzeneazoglyoxaline on reduction with stannous chloride, the principal product of the reaction being 2-amino-5-p-aminophenyl-4-methylglyoxaline (XVII), a compound having similar properties to 2-amino-4-p-aminophenylglyoxaline.



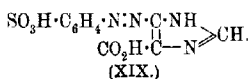
The constitution of 5-benzeneazo-4-methylglyoxaline (XVIII) could not be proved directly as in the case of the 2-isomeride. On reduction, aniline and a considerable amount of ammonia were formed, together with other products, which included a base,  $\text{C}_6\text{H}_{10}\text{ON}_2$  (p. 254), when stannous chloride was employed as the reducing agent, and a base,  $\text{C}_{10}\text{H}_{11}\text{ON}_3$  (p. 255), when zinc dust and acetic acid were used. The disintegration of the molecule indicated by the formation of ammonia is similar to that occurring in the reduction of the 4-nitroglyoxalines, and affords evidence that the constitution of the compound is represented correctly by the formula of 5-benzeneazo-4-methylglyoxaline. The formula is supported by the fact that the compound is soluble in dilute aqueous sodium hydroxide, which indicates that the imino-group is unsubstituted. Moreover, it is fairly stable towards boiling dilute acids. Its properties are not therefore in accord with those of a compound represented by the alternative formula, 1-benzeneazo-4-methylglyoxaline.

That aryldiazonium salts are capable of substituting the 4-position of the glyoxaline ring follows from the reduction of 2-phenyl-

4-*p*-bromobenzeneazoglyoxaline,  $C_{15}H_{11}N_4Br$ , for a compound,  $C_{15}H_{13}N_4Br$ , is produced, which is evidently derived from the corresponding hydrazo-compound by a change of the semidine or benzidine type (compare p. 257).

The polyarylazoglyoxalines—2:4:5-trisbenzeneazoglyoxaline and 2:5-bisbenzeneazo-4-methylglyoxaline—are insoluble in dilute mineral acids, and are decomposed on boiling with 10 per cent. hydrochloric acid. Nevertheless, we regard them as *C*-azo-compounds, because they are soluble to some extent in aqueous sodium hydroxide. In the case of the second compound, we have established the fact that it is precipitated unchanged from its solution in aqueous sodium hydroxide by means of acetic acid. The fact that the number of arylazo-groups in the polyarylazo-compounds corresponds with the number of nuclear methine groups in the parent glyoxaline points in the same direction.

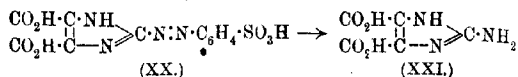
The interaction of glyoxaline-4:5-dicarboxylic acid and diazobenzene-*p*-sulphonic acid was studied by Burian (*loc. cit.*), who found that carbon dioxide was liberated, and described a product forming yellow needles or red, microscopic prisms which gave on analysis results indicating that it was a compound derived from one molecular proportion of diazobenzene-*p*-sulphonic acid and one of glyoxaline-4-carboxylic acid,  $SO_3H \cdot C_6H_4 \cdot N \cdot N \cdot C_3H_2N_2 \cdot CO_2H$ . Burian regarded this as a 1-substituted arylazoglyoxaline, but we thought it more probable that the arylazo-group had displaced a carboxyl group in the 4-(or 5)-position, and that the compound was 5-*p*-sulphobenzeneazoglyoxaline-4-carboxylic acid (XIX).



This compound would yield 5-aminoglyoxaline-4-carboxylic acid if a suitable method of reduction could be found, and we therefore attempted to repeat its preparation, but were unable to do so. We can confirm Burian's statement that carbon dioxide is liberated in the reaction, but find the yield of this to be only about 40 per cent. of the theoretical, much less than he states. Moreover, we have isolated in a yield of about 30 per cent. of the theoretical the condensation product of diazobenzene-*p*-sulphonic acid and glyoxaline-4:5-dicarboxylic acid, namely, 2-*p*-sulphobenzeneazoglyoxaline-4:5-dicarboxylic acid (XX). No other definite compound could be isolated from the reaction mixture, and it appears to us that the compound described by Burian was probably a mixture of our acid with its sodium salt.

2-*p*-Sulphobenzeneazoglyoxaline-4:5-dicarboxylic acid yields on

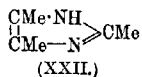
reduction with sodium hyposulphite, sulphanilic acid and 2-amino-glyoxaline-4:5-dicarboxylic acid (XXI).



With the object of eliminating the elements of carbon dioxide, this acid was heated with water for twelve hours at 170°, when carbon dioxide and approximately one molecular proportion of ammonia were liberated, but no other fission product could be identified. On the other hand, when boiled with aniline for six hours, it gave a quantity of 2-aminoglyoxaline.

Whilst we were unable to isolate 5-*p*-sulphobenzeneazoglyoxaline-4-carboxylic acid (XIX) from the products of the interaction of diazobenzene-*p*-sulphonic acid and glyoxaline-4:5 dicarboxylic acid, the liberation of carbon dioxide indicates that substitution in the 4-(or 5-)position takes place to some extent. Moreover, we can confirm the fact that 2-methylglyoxaline-4:5-dicarboxylic acid couples with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate.

On the other hand, 2:4:5-trimethylglyoxaline (XXII), which contains a free imino-group but no other hydrogen atom attached



to the nucleus, does not couple with sodium diazobenzene-*p*-sulphonate. Further, a striking difference is exhibited between the facilities with which 2-amino-4-*p*-aminophenylglyoxaline (VI) containing a displaceable hydrogen atom in the glyoxaline nucleus and its methyl homologue (XVII) react with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate. The first gives the characteristic intense cherry-red colour immediately, whilst the second gives a pale orange colour which deepens on keeping, and is probably due to the participation of the aminophenyl group.

On reviewing these results and those of previous investigators, it appears to us that glyoxalines, in order to be capable of coupling, must contain a free imino-group and also a hydrogen atom, or some other displaceable group, such as the carboxyl group, in one of the 2-, 4-, or 5-positions, and that the arylazoglyoxalines hitherto prepared are *U*-azo-compounds.

The literature of the arylazoglyoxalines contains one possible exception to this generalisation—the compound (orange needles melting at 120–122°) described by Burian (*loc. cit.*) as having been obtained by the action of diazotised benzidine on 2-thiol-4:5-

diphenylglyoxaline. Since we found that 2-thiol-4:5-dimethylglyoxaline and 2-thiol-4:5-diphenylglyoxaline only gave pale orange colorations with sodium diazobenzene-*p*-sulphonate, we repeated Burian's preparation. We failed, however, to confirm his results, but isolated from the product, as main constituents, much unchanged 2-thiol-4:5-diphenylglyoxaline and a reddish-brown, amorphous compound, melting and decomposing above 200°, which from its low nitrogen content (5.5 per cent.) and the ratio of nitrogen to sulphur (2:1) could not have been an arylazo-derivative derived from 2-thiol-4:5-diphenylglyoxaline.

#### EXPERIMENTAL.

##### *Part I. Glyoxalines and their Carboxylic Acids.*

##### *Preparation of Glyoxaline-4:5-dicarboxylic Acid.*

Twenty-five grams of finely powdered tartaric acid are dissolved in 108 c.c. of nitric acid (D 1.5), and 125 c.c. of sulphuric acid are added. The mixture, which attains a temperature of about 40°, soon begins to deposit crystals, and is kept for three to four hours in a cool place. The nitrotartaric acid is collected, washed with 50 per cent. sulphuric acid, drained on porous porcelain, and stirred immediately with 150 grams of powdered ice until dissolved, when the temperature falls to -5°.

The liquid is immersed in a freezing mixture, and 100 c.c. of aqueous ammonia (D 0.880) are added gradually, the temperature being kept below 0°. Then 50 c.c. of 40 per cent. aqueous formaldehyde are added slowly, keeping the temperature below 10°. The product is removed from the freezing mixture after three to four hours, and kept overnight. It is then mixed with a little alcohol and acidified with hydrochloric acid, when 15.5 to 16.0 grams of glyoxaline-4:5-dicarboxylic acid separate, that is, about 60 per cent. of the theoretical yield calculated on the quantity of tartaric acid employed.

Glyoxaline-4:5-dicarboxylic acid melts and effervesces at 288° (corr.). It is soluble in about 800 parts of boiling water and in about 2000 parts of cold water. It is practically insoluble in the usual organic solvents, but dissolves sparingly in pyridine. It is soluble in concentrated mineral acids, but is precipitated unchanged on dilution with water. The *monosodium* salt, which crystallises from water as a felted mass of feathery needles containing 1H<sub>2</sub>O (Found: H<sub>2</sub>O=9.4; in dried salt, Na=12.8. Calc.: H<sub>2</sub>O=9.2; Na=12.9 per cent.), is sparingly soluble in water but readily so in aqueous sodium hydr-

oxide, probably owing to the formation of a disodium salt in solution. Moreover, the addition of alcohol to a solution of the acid in sufficient aqueous sodium hydroxide to form the disodium salt causes the precipitation of a granular deposit approximating in composition to the disodium salt. (Found, in salt dried at  $110^{\circ}$ , Na = 21.2.  $C_6H_2O_7N_2Na_2$  requires Na = 23.0 per cent.)

The acid is very stable towards nitric acid; after boiling it with ten times its weight of concentrated nitric acid for twenty-four hours, more than 90 per cent. was recovered unchanged, whilst similar results were obtained in a sealed tube at  $130^{\circ}$ , and when the acid was boiled with equal parts of nitric and sulphuric acids.

The acid is very resistant to esterification, for, after boiling with alcoholic sulphuric acid for twenty-four hours, 95 per cent. was recovered unchanged.

#### *The Preparation of Glyoxaline.*

One hundred grams of glyoxaline-4:5-dicarboxylic acid were distilled, under normal pressure, in quantities of 4 grams from a small flask into a long, wide air condenser. The distillate, which had solidified in the condenser, was crystallised from benzene, and gave a 92 per cent. yield of the pure base.

*Glyoxaline picrate* crystallises from water in long, fine, yellow needles, which become orange on drying at  $100^{\circ}$ , and then melt at  $212^{\circ}$  (corr.), after sintering from  $208^{\circ}$ . It contains rather more than  $1H_2O$  (Found, loss at  $100^{\circ}$  = 7.2; in substance dried at  $100^{\circ}$ , N = 23.3.  $C_3H_4N_2 \cdot C_6H_3O_7N_3$  [297.1] requires N = 23.6 per cent.).

*Glyoxaline hydrogen tartrate* crystallises from water in fine prisms of characteristic trapezoidal shape, which are anhydrous and melt at  $202^{\circ}$  (corr.). It is readily soluble in cold water, and is best crystallised from 50 per cent. alcohol (Found: N = 12.8.  $C_3H_4N_2 \cdot C_4H_6O_6$  [218.1] requires N = 12.8 per cent.).

Glyoxaline hydrogen oxalate crystallises from water as a felted mass of prismatic needles, which are anhydrous and melt at  $233^{\circ}$  (corr.) after sintering from  $230^{\circ}$ . It is soluble in five or six parts of boiling water, and much less so in cold water (Found: N = 17.8. Calc.: N = 17.7 per cent.).

#### *Action of Boiling Aniline on Glyoxaline-4:5-dicarboxylic Acid: Formation of Glyoxaline-4-carboxyanilide and Glyoxaline.*

Five grams of glyoxaline-4:5-dicarboxylic acid were boiled with 50 c.c. of aniline for nine hours under a reflux condenser, when

the acid gradually passed into solution. The product was mixed with water and subjected to distillation with steam until the excess of aniline had been removed. The residual aqueous solution was filtered from a small quantity of resinous matter whilst still hot, when the filtrate at once began to deposit the anilide as a felted mass of fine needles. The first crop amounted to 2.6 grams, and a further quantity of 0.1 gram was obtained on concentrating the mother liquor. The filtrate from this gave on acidification 0.1 gram of glyoxaline-4:5-dicarboxylic acid, but no glyoxaline-4-carboxylic acid was found. The final mother liquor when mixed with sodium carbonate, evaporated to dryness, and extracted with benzene gave 0.9 gram of glyoxaline.

*Glyoxaline-4-carboxyanilide* crystallises from boiling water in fine, colourless needles, which are anhydrous and melt at 227–228° (corr.). It is fairly readily soluble in alcohol, but only sparingly so in boiling water and the other usual organic solvents.

Found: C=64.2; H=5.1; N=22.6.

$C_{10}H_8ON_2$  (187.15) requires C=64.2; H=4.9; N=22.5 per cent.

*Hydrolysis of the Anilide.*—The anilide is only slowly hydrolysed by 10 per cent. hydrochloric acid at 100°, but more readily at 130°.

One gram of the anilide was heated with 10 c.c. of 10 per cent. hydrochloric acid at 130° for three hours. The resulting solution was evaporated to dryness to remove the excess of acid, the residue dissolved in water, basified with sodium carbonate, and extracted with ether to remove aniline. Sufficient hydrochloric acid was added to render the solution faintly acid to methyl-orange, when crystallisation set in almost immediately, and 0.42 gram of glyoxaline-4-carboxylic acid was isolated. The properties of the acid and its hydrochloride, nitrate, and picrate agreed with those previously given (T., 1916, 109, 199) for the acid prepared by the oxidation of 4-hydroxymethylglyoxaline, and the melting points of mixtures of the compounds from the two sources were not depressed.

#### 2-Methylglyoxaline-4:5-dicarboxylic Acid.

This acid was prepared in an analogous manner to its lower homologue, employing a solution of 15 c.c. of freshly distilled acetaldehyde dissolved in 50 c.c. of ice-water in the place of the aqueous formaldehyde. The yield of 2-methylglyoxaline-4:5-dicarboxylic acid, containing  $1H_2O$ , obtained from 25 grams of tartaric acid was 22 grams, that is, 67 per cent. of the theoretical.



Maquenne (*loc. cit.*) obtained 50 grams of the product from 100 grams of tartaric acid, that is, 38 per cent. of the theoretical.

Generally, the properties of this acid are very similar to those of glyoxaline-4:5-dicarboxylic acid, and it behaves similarly on acid and alkaline hydrolysis.

With sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate, it gives a faint red colour which deepens on keeping, whilst glyoxaline-4:5-dicarboxylic acid gives a deeper red colour in the first instance.

*Action of Boiling Aniline on 2-Methylglyoxaline-4:5-dicarboxylic Acid.*

Twenty grams of hydrated 2-methylglyoxaline-4:5-dicarboxylic acid, when treated with boiling aniline under the same conditions as its lower homologue, gave 11 grams of the hydrated anilide of 2-methylglyoxaline-4-carboxylic acid and 3.8 grams of 2-methylglyoxaline.

2-Methylglyoxaline-4-carboxyanilide crystallises from boiling water as a felted mass of colourless, silky needles, which contain rather less than  $11\text{H}_2\text{O}$ . It is sparingly soluble in boiling water, but readily so in alcohol. After drying at  $110^\circ$ , it melts at  $208^\circ$  (corr.).

Found, loss at  $110^\circ$  in three samples = 6.9, 7.0, 7.2.

$\text{C}_{11}\text{H}_{11}\text{ON}_3 \cdot \text{H}_2\text{O}$  requires  $\text{H}_2\text{O}$  = 8.2 per cent.

Found, in substance dried at  $110^\circ$ , C = 65.1, 65.6; H = 5.7, 5.6; N = 20.9.

$\text{C}_{11}\text{H}_{11}\text{ON}_3$  (201.2) requires C = 65.6; H = 5.5; N = 20.9 per cent.

2-Methylglyoxaline-4-carboxylic acid is obtained in nearly the theoretical yield by the hydrolysis of its anilide under similar conditions to those already described for glyoxaline-4-carboxylic acid. When placed in a bath at  $250^\circ$ , it melts and effervesces at  $262^\circ$  (corr.). It crystallises from water in clusters of prismatic needles containing  $11\text{H}_2\text{O}$ . It is soluble in about twenty parts of boiling water, but is practically insoluble in the usual organic solvents.

Found, loss at  $110^\circ$  = 12.9.

$\text{C}_5\text{H}_6\text{O}_2\text{N}_2 \cdot \text{H}_2\text{O}$  requires  $\text{H}_2\text{O}$  = 12.5 per cent.

Found, in the substance dried at  $110^\circ$ , C = 47.3; H = 4.8; N = 21.9.

$\text{C}_5\text{H}_6\text{O}_2\text{N}_2$  (126.1) requires C = 47.6; H = 4.8; N = 22.2 per cent.

With sodium diazobenzene-*p*-sulphonate it gives a red colour in sodium carbonate solution.

The hydrochloride crystallises from water, in which it is readily

soluble, in minute, flattened, rhombic prisms, which are anhydrous. It melts and effervesces at  $268^{\circ}$  (corr.).

Found: N=16.9; Cl=21.5.

$C_5H_6O_2N_2 \cdot HCl$  (162.6) requires N=17.2; Cl=21.8 per cent.

The *nitrate* crystallises from water, in which it is very readily soluble, in minute rhombic prisms, which melt and effervesce at  $190^{\circ}$  (corr.), resolidify, and on further heating gradually darken, melting at about  $240^{\circ}$ .

Found: C=31.7; H=4.1.

$C_5H_6O_2N_2 \cdot HNO_3$  (189.1) requires C=31.7; H=3.7 per cent.

The *picrate* crystallises from water in minute cubes containing  $2H_2O$ , which is lost at  $100^{\circ}$  (Found:  $H_2O$ =9.4. Calc. for  $2H_2O$ , 9.2 per cent.). It melts to a turbid liquid at  $200^{\circ}$  (corr.), which does not become clear until  $224^{\circ}$ , at which temperature effervescence begins.

Found, in salt dried at  $100^{\circ}$ , N=19.4.

$C_5H_6O_2N_2 \cdot C_6H_3O_7N_3$  (355.2) requires N=19.7 per cent.

*2-Methylglyoxaline picrate* crystallises from boiling water in fine needles, which are anhydrous and melt at  $213^{\circ}$  (corr.).

Found: N=22.3.

$C_4H_6N_2 \cdot C_6H_3O_7N_3$  (311.2) requires N=22.5 per cent.

*2-Methylglyoxaline hydrogen oxalate* crystallises from water in large, rhombic prisms which contain  $2H_2O$  (Found:  $H_2O$ =17.6. Calc. for  $2H_2O$ :  $H_2O$ =17.3 per cent.). After drying at  $100^{\circ}$ , it melts at  $160^{\circ}$  (corr.), and effervesces on further heating. It is much more readily soluble in water than the corresponding glyoxaline salt.

Found, in dried salt: N=16.1.

$C_4H_6N_2 \cdot C_2H_2O_4$  (172.1) requires N=16.3 per cent.

#### *2-Ethylglyoxaline-4:5-dicarboxylic Acid.*

This acid was prepared in the same way as the methyl substituted acid. From 32 c.c. of propaldehyde, and the nitrotartaric acid obtained from 50 grams of tartaric acid, 43 grams of hydrated *2-ethylglyoxaline-4:5-dicarboxylic acid* were obtained, that is, 64 per cent. of the theoretical yield; Maquenne obtained 30 per cent. *2-Ethylglyoxaline-4:5-dicarboxylic acid* melts and effervesces at  $259^{\circ}$  (corr.).

*2-Phenyglyoxaline-4:5-dicarboxylic Acid.*

The nitrotartaric acid from 25 grams of tartaric acid was treated with 100 c.c. of aqueous ammonia in the manner previously described. Then 20 grams of benzaldehyde were added, with stirring, below  $0^{\circ}$ , and the stirring was continued for seven hours, the temperature of the mixture being gradually allowed to approach that of the room. After keeping overnight, 17.1 grams of 2-phenyglyoxaline-4:5-dicarboxylic acid were isolated, that is, 48 per cent. of the theoretical yield, whereas Maquenne's yield was only 8 per cent. 2-Phenyglyoxaline-4:5-dicarboxylic acid melts and effervesces at  $271^{\circ}$  (corr.).

When distilled under the conditions previously described in the case of glyoxaline-4:5-dicarboxylic acid, it gives 2-phenyglyoxaline in a yield of more than 80 per cent. of the theoretical.

2-Phenyglyoxaline crystallises from water in small, prismatic needles, which melt at  $148-149^{\circ}$  (corr.) and are anhydrous.

2-Phenyglyoxaline nitrate is readily soluble in water, but less so in alcohol, from which it separates in leaflets containing  $\frac{1}{2}\text{H}_2\text{O}$ , which is lost at  $60^{\circ}$  in a vacuum. The dried salt melts at  $135^{\circ}$  (corr.).

Found, in air-dried salt,  $\text{H}_2\text{O}=6.1$ ; in dried salt,  $\text{N}=20.0$ .

$\text{C}_9\text{H}_8\text{N}_2, \text{HNO}_3$  (207.1) requires  $\text{N}=20.3$  per cent.

The *hydrogen oxalate* crystallises from water in flattened needles, which melt and effervesce at  $219^{\circ}$  (corr.), and are anhydrous. It is readily soluble in hot water, but less so in cold.

Found:  $\text{N}=12.0$ .

$\text{C}_9\text{H}_8\text{N}_2, \text{C}_2\text{H}_2\text{O}_4$  (234.1) requires  $\text{N}=12.0$  per cent.

The *picrate* is sparingly soluble even in boiling water, from which it crystallises in fine needles which melt at  $238^{\circ}$  (corr.), and are anhydrous.

Found:  $\text{N}=18.6$ .

$\text{C}_9\text{H}_8\text{N}_2, \text{C}_6\text{H}_3\text{O}_7\text{N}_3$  (373.2) requires  $\text{N}=18.8$  per cent.

*4:5-Dimethyl- and 2:4:5-Trimethyl-glyoxaline.*

When 4:5-dimethylglyoxaline is prepared by Windaus' method (*Ber.*, 1909, **42**, 758), it is contaminated with 2:4:5-trimethylglyoxaline, which results from the interaction of diacetyl and ammonia (von Pechmann, *Ber.*, 1888, **21**, 1414).

8.6 Grams of diacetyl were dissolved in 50 c.c. of water, 50 c.c. of 40 per cent. aqueous formaldehyde added, the mixture cooled to  $0^{\circ}$ , and 80 c.c. of concentrated ammonia solution gradually

added, the reaction mixture being stirred and kept below  $0^{\circ}$ . After the addition was ended, the mixture was allowed to remain in a cool place overnight, then evaporated to a low bulk, saturated with anhydrous potassium carbonate, and the oil which separated extracted by ether. The crude extract, which was contaminated with hexamine, amounted to 5.9 grams. After destruction of the hexamethylenetetramine by boiling dilute hydrochloric acid, the picrates of the constituent bases were fractionated from water, when 5.7 grams of 4:5-dimethylglyoxaline picrate (17.5 per cent. of the theoretical yield) were obtained first, and then 3.5 grams of 2:4:5-trimethylglyoxaline picrate.

2:4:5-Trimethylglyoxaline picrate sinters from  $160^{\circ}$  and melts at  $163^{\circ}$  (corr.). It crystallises from water in well-defined prisms, which are often serrated.

Found: N=20.6.

$C_6H_{10}N_2, C_6H_3O_7N_3$  requires N=20.6 per cent.

The hydrochloride, previously prepared by von Pechmann, crystallises from alcohol in fine needles, which are anhydrous and melt at  $316^{\circ}$  (corr.) (Found: N=19.0; Cl=24.2. Calc.: N=19.1; Cl=24.2 per cent.).

4:5-Dimethylglyoxaline hydrochloride crystallises from alcohol in well-defined, rhombic prisms which melt and decompose at  $305^{\circ}$  (corr.).

Found: N=21.1; Cl=26.4.

$C_6H_8N_2, HCl$  requires N=21.1; Cl=26.7 per cent.

4:5-Dimethylglyoxaline was also prepared by a modification of Künne's method (*Ber.*, 1895, **28**, 2039; compare also Jowett, T., 1905, **87**, 407). Nine grams of methyl  $\alpha$ -isonitrosoethyl ketone were reduced with stannous chloride, as described by Künne, but the temperature of the reaction mixture was maintained at  $15^{\circ}$ , and, after the removal of the tin, the evaporation of the liquor was conducted entirely under diminished pressure. By these means, a yield of 10 grams of crude, crystalline methyl  $\alpha$ -aminoethyl ketone hydrochloride was obtained, as against 4.2 grams of syrup obtained by Künne. When this product was heated on the water-bath for four hours with 10 grams of potassium thiocyanate and 40 c.c. of water, 5.2 grams of 2-thiol-4:5-dimethylglyoxaline separated, and this gave 4:5-dimethylglyoxaline picrate in a yield of 85 per cent. of the theoretical when oxidised with the calculated quantity of ferric chloride.\* The yield of 4:5-dimethylglyoxaline from methyl ethyl ketone is thus 23.8 per cent. of the theoretical.

\* The method of oxidising thiolglyoxalines to glyoxalines by means of ferric chloride has been described by one of us (T., 1911, **99**, 2175) in the case of

*Part II. Nitroglyoxalines.**4-Nitroglyoxaline.*

Rung and Behrend (*loc. cit.*) prepared 4-nitroglyoxaline in a yield of 36 per cent. of the theoretical by boiling glyoxaline with a mixture of nitric and sulphuric acids. The yield can be improved greatly by the method given below. Eight grams of glyoxaline were dissolved in 16 c.c. of nitric acid (D 1.4), cooled, and 16 c.c. of sulphuric acid cautiously added. A vigorous reaction ensued, and when this had subsided the mixture was boiled gently for two hours, allowed to cool, and then poured into ice-water, when 7.85 grams of 4-nitroglyoxaline separated. The mother liquors yielded a further 0.5 gram of 4-nitroglyoxaline identical with the above, but no glyoxaline and merely a trace of other crystalline material. The total yield of 4-nitroglyoxaline thus amounted to 63 per cent. of the theoretical. 4-Nitroglyoxaline crystallises from boiling acetic acid or from alcohol in stout, rhombic prisms, which are anhydrous and melt at  $312-313^{\circ}$  (corr.) (Found: N=36.8. Calc.: N=37.1 per cent.). It is only very sparingly soluble in boiling water. Although it dissolves in strong mineral acids, it is precipitated unchanged on the addition of water, and is recovered unchanged when crystallised from aqueous picric acid.

4-Nitro-2-methylglyoxaline was similarly prepared. It crystallises from water in fine needles, which are anhydrous and melt at  $254^{\circ}$  (corr.), sintering from  $251^{\circ}$ .

Found: N=33.0.

$C_4H_5O_2N_3$  (127.1) requires N=33.1 per cent.

5-Nitro-4-methylglyoxaline was prepared by Windaus (*loc. cit.*) in a 60 per cent. yield by warming 4-methylglyoxaline with fuming nitric acid at  $80^{\circ}$ . Using this method, we found the main product to be 4-methylglyoxaline nitrate. Proceeding according to the method described for 4-nitro-2-methylglyoxaline, 5 grams of 4-methylglyoxaline gave 7 grams of 5-nitro-4-methylglyoxaline (Found: N=32.8. Calc.: N=33.1 per cent.) melting at  $248^{\circ}$  (corr.), that is, 90 per cent. of the theoretical yield.

2-thiol-4-aminomethylglyoxaline. The low yield of 4-aminomethylglyoxaline recorded (56 per cent. of the theoretical) was due to the fact that insufficient ferric chloride had been employed. When the calculated quantity (16.2 grams) of this reagent is used, the product is obtained in a yield of 90 per cent. of the theoretical.

*Attempted Nitration of 4:5-Dimethylglyoxaline.*

To five grams of 4:5-dimethylglyoxaline dissolved in 15 c.c. of nitric acid (D 1.4), 15 c.c. of sulphuric acid were added. The first vigorous reaction was controlled by cooling, and after it had ended the mixture was heated for two hours on the water-bath. From the reaction product, 1.7 grams of 4:5-dimethylglyoxaline were recovered, together with 0.3 gram of the nitrate of 4-methylglyoxaline-5-carboxylic acid (Found: C=32.1; H=4.0; N=21.7. Calc.: C=31.6; H=3.7; N=22.1 per cent.), which deposited the corresponding acid, melting and effervescing at 222°, on the addition of the calculated quantity of sodium hydroxide. From the pure acid, the hydrochloride, which melted and decomposed at 231°, and the nitrate, which decomposed at 189°, were prepared. The melting points of the acid and its salts are in agreement with those found by Gerngross (*loc. cit.*) for 4-methylglyoxaline-5-carboxylic acid.

*Reduction of Nitroglyoxalines with Tin and Hydrochloric Acid.*

When 4-nitroglyoxaline, 4-nitro-2-methylglyoxaline, or 5-nitro-4-methylglyoxaline is reduced with tin and hydrochloric acid, and the product mixed with sodium hydroxide and distilled into standard acid, two of the three atoms of nitrogen present in the molecule are eliminated in the form of ammonia:

0.5609 of 4-nitroglyoxaline gave 0.1746  $\text{NH}_3$ ; calc. as above, 0.1688.

0.4292 of 4-nitro-2-methylglyoxaline gave 0.118  $\text{NH}_3$ ; calc. as above, 0.115.

0.4931 of 5-nitro-4-methylglyoxaline gave 0.1378  $\text{NH}_3$ ; calc. as above, 0.1320.

That the greater part of the ammonia is actually produced during the reduction, and not by the subsequent action of the alkali, is shown in the case of 4-nitroglyoxaline by the following experiment.

Twelve grams of 4-nitroglyoxaline were reduced by means of tin and hydrochloric acid in the usual manner. The reduced quors were freed from tin and then evaporated to dryness, then moistened with alcohol, and again evaporated to remove water as far as possible. The crude product was extracted with alcohol and left 9 grams of a crystalline solid, which proved to be ammonium chloride (Found: N=25.9; Cl=66.0. Calc.: N=26.2;

$\text{Cl} = 66.3$  per cent.). The residue of the purple alcoholic solution gave 5 grams of an insoluble phosphotungstate after the removal of ammonia. This product has not yet been investigated.

*Reduction of Nitroglyoxalines with Sodium Hyposulphite.*

Behrend and Schmitz (*loc. cit.*) observed that 4-nitroglyoxaline gave a beautiful blue dye when treated with alkaline reducing agents. We can confirm this result, but find that ammonia is also produced in an amount corresponding with the loss of two atoms of nitrogen in this form from three molecules of 4-nitroglyoxaline when this compound is reduced with sodium hyposulphite in aqueous sodium hydroxide:

0.5148 of 4-nitroglyoxaline gave 0.0521  $\text{NH}_3$ ; calc. as above, 0.0516.

The liquors remaining from the distillation gradually acquired a dark blue colour on exposure to the air, and on acidification with acetic acid deposited rather less than 0.1 gram of a blue compound which did not melt below  $300^\circ$ .

The reduction of 5-nitro-4-methylglyoxaline with alkaline sodium hyposulphite led to the same result as in the case of 4-nitroglyoxaline, two molecules of ammonia being produced from three molecules of the nitro-compound (0.5311 gave 0.0487  $\text{NH}_3$ ; calc. as above, 0.0474). The reduced solution gradually acquired a rose colour on exposure to air, but gave no precipitate with acetic acid.

4-Nitro-2-methylglyoxaline behaved differently from the above compounds on reduction with alkaline sodium hyposulphite, yielding one molecule of ammonia from three molecules of the nitro-compound (0.5084 gave 0.0230  $\text{NH}_3$ ; calc. as above, 0.0227).

*Part III. Arylazoglyoxalines.*

*2-Benzeneazoglyoxaline (IV, p. 221).*

23.25 Grams of aniline were dissolved in 62.5 c.c. of hydrochloric acid and 187.5 c.c. of water, and diazotised with 18 grams of sodium nitrite dissolved in 100 c.c. of water. The solution was run slowly into a well-stirred solution of 17 grams of glyoxaline and 40 grams of anhydrous sodium carbonate in 1250 c.c. of water, previously cooled to  $5^\circ$ , and kept overnight. The insoluble orange powder was collected, washed well with water, and extracted successively with 250, 125, and 125 c.c. of cold 2.5 per cent. hydrochloric acid. (Extract = 4.) The insoluble material amounted to 4.4

grams, and after crystallisation from alcohol gave 2:4:5-*tris-benzeneazoglyoxaline*, of which only 0.5 gram was obtained in a pure state. This compound decomposes at about 200° and effervesces at 208° (corr.). When pure, it is only sparingly soluble even in boiling alcohol, from which it crystallises slowly in dark brown clusters of crystals of indeterminate shape. (0.84 required 60 c.c. of boiling alcohol.)

Found: C=66.0; H=4.6; N=29.0.

$C_{21}H_{16}N_8$  (380.3) requires C=66.3; H=4.2; N=29.5 per cent.

Trisbenzeneazoglyoxaline is insoluble in cold dilute hydrochloric acid, and is decomposed when boiled with this reagent. It dissolves to some extent in aqueous sodium hydroxide.

The hydrochloric acid extract (4) was diluted with water and basified with sodium carbonate, when crude 2-benzeneazoglyoxaline was obtained as a yellow, crystalline precipitate, which, after thorough washing with cold water and drying, amounted to 34 grams. On crystallisation from 150 c.c. of alcohol, 31 grams of the pure base were obtained, that is, 74 per cent. of the theoretical. No other definite compound could be isolated from the mother liquor.

2-Benzeneazoglyoxaline crystallises from alcohol in large, orange tablets resembling potassium dichromate in appearance. It melts at 190° (corr.) to a reddish-black liquid.

Found: C=62.7, 62.7; H=4.8, 4.9; N=32.3

$C_9H_8N_4$  (172.1) requires C=62.8; H=4.7; N=32.6 per cent.

*Rung and Behrend's Method.*—By this method, in which benzenediazonium chloride is allowed to react with glyoxaline without the addition of alkali, 5 grams of glyoxaline gave 3.3 grams of crude precipitate insoluble in water. Of this, 2.2 grams were separated into 0.7 gram of insoluble resin, which appeared to evolve gas on keeping, and 1.45 grams soluble in acid, which gave pure 2-benzeneazoglyoxaline on crystallisation from alcohol. The crude precipitate was less readily purified by direct crystallisation from alcohol.

*General Properties of Arylazoglyoxalines.*—To avoid repetition, it will be convenient to describe the general properties of the monoarylazoglyoxalines at this point. 2-Benzeneazoglyoxaline and 2-benzeneazo-4-methylglyoxaline are fairly readily soluble in alcohol, ethyl acetate, or acetone, sparingly so in ether, chloroform, or benzene. 5-Benzeneazo-4-methylglyoxaline, 2-*p*-bromobenzenazoglyoxaline, and 4-*p*-bromobenzenazo-2-methylglyoxaline are sparingly soluble in the first three solvents and very sparingly so in the last three.



These compounds are almost insoluble in cold water or in dilute aqueous ammonia or sodium carbonate, but dissolve to some extent in dilute aqueous sodium hydroxide. The benzeneazo-compounds dissolve readily in dilute hydrochloric acid, and the solutions yield crystalline hydrochlorides on concentration; the hydrochlorides of the *p*-bromobenzeneazo-compounds are sparingly soluble in water.

The stability of a 2- and a 4-substituted member of the group towards boiling dilute hydrochloric acid was examined. When 0.5 gram of 2-benzeneazoglyoxaline was boiled with 20 c.c. of 10 per cent. aqueous hydrochloric acid for two hours under a reflux condenser, 0.35 gram was recovered little changed on the addition of ammonia, and readily gave the starting material in a pure state on crystallisation from alcohol.

When 5-benzeneazo-4-methylglyoxaline was boiled with an excess of 10 per cent. aqueous hydrochloric acid for a few minutes, it was recovered unchanged after the addition of ammonia, but after boiling for one hour it was mainly decomposed, with the formation of resinous compounds.

The arylazoglyoxalines dissolve in concentrated sulphuric acid, giving bright-coloured solutions. The monoarylaazo-derivatives yield mainly orange or magenta solutions, the 2-substituted derivatives being more intensely coloured than the 4-substituted compounds, whilst the solutions of bis- and tris-arylazoglyoxalines are green and still more intense than those of the 2-monoarylaazo-derivatives.

*Reduction of 2-Benzeneazoglyoxaline with Stannous Chloride:*

*Isolation of 2-Amino-4-p-aminophenylglyoxaline, 2-Aminoglyoxaline, Guanidine, and Aniline.*

Twenty grams of 2-benzeneazoglyoxaline were dissolved in 200 c.c. of boiling 2.5 per cent. hydrochloric acid and mixed with 120 c.c. of stannous chloride solution.\* The solution was immediately decolorised, and when mixed with 200 c.c. of hydrochloric acid deposited a crystalline tin salt (A). This was collected, and the mother liquor was evaporated to dryness, dissolved in hot water, and freed from tin. It was then evaporated to low bulk, mixed with sodium carbonate, and extracted with ether, which removed 3.0 grams of crude aniline. The alkaline liquor was acidified faintly with hydrochloric acid, evaporated to dryness, and extracted with alcohol, when 3.1 grams of extract were obtained. This was

\* The stannous chloride solution employed throughout this investigation was made by mixing 40 grams of "tin salt" with sufficient hydrochloric acid to make 100 c.c. of solution.

mixed with stannic chloride, and deposited, first, 2.2 grams of pure *2-aminoglyoxaline stannichloride*, then crops of the crude salt, from which a further quantity of 1.0 gram of the pure salt was obtained, the total yield amounting to 11 per cent. of the theoretical. The final stannichloride mother liquors were deprived of tin by means of hydrogen sulphide and mixed with picric acid. After crystallisation from water, the first crop of picrate, which melted at  $325^{\circ}$ , was decomposed by sulphuric acid, the picric acid being removed by means of ether. The solution of sulphates was deprived of sulphuric acid by barium hydroxide, and from excess of this reagent by carbon dioxide. The resulting solution was neutralised with aqueous oxalic acid, mixed with as much more aqueous oxalic acid, and concentrated, when crude guanidine hydrogen oxalate separated. After recrystallisation from water, this amounted to 0.7 gram, melting and effervescing at  $172-173^{\circ}$  (corr.) alone or when mixed with pure guanidine hydrogen oxalate.

The crystalline tin salt (A) was dissolved in water, treated with hydrogen sulphide, filtered from tin sulphide, and concentrated, when 18.55 grams of *2-amino-4-p-aminophenylglyoxaline dihydrochloride* separated, that is, 64.6 per cent. of the theoretical yield.

*2-Amino-4-p-aminophenylglyoxaline*,  $C_9H_{10}N_4$  (VI, p. 222).

When the dihydrochloride is mixed with an equivalent quantity of sodium carbonate, a colourless oil separates which solidifies on keeping. This is a carbonate, for it effervesces on treatment with acid, and when dissolved in boiling water disengages carbon dioxide vigorously on the addition of animal charcoal, leaving a solution of the free base, which crystallises on keeping. This solution becomes brown at the top owing to oxidation in the air, whilst the amine becomes mauve where exposed to the light.

To 5.0 grams of the dihydrochloride in 50 c.c. of boiling water, 30 c.c. of hot 10 per cent. aqueous sodium carbonate and a pinch of animal charcoal were added. The solution was boiled for five minutes, filtered, and kept, when 3.1 grams of the base separated and were recrystallised from water. This base crystallises from water in glistening leaflets which melt and effervesce at  $148^{\circ}$  (corr.). It contains  $1H_2O$ , which is not lost in a vacuum or on heating at  $100^{\circ}$ .

Found: C=56.3; H=6.4; N=29.5, 29.2.

$C_9H_{10}N_4 \cdot H_2O$  (192.2) requires C=56.2; H=6.3; N=29.2 per cent.

It is sparingly soluble in cold, fairly readily so in hot water; fairly readily soluble in cold, readily in hot alcohol, and very sparingly so in chloroform or ether.

An aqueous solution of the base gives, with silver nitrate, a white precipitate, which blackens at once on the addition of ammonia; with Fehling's solution, a nearly black precipitate—presumably a copper salt—which is unchanged on boiling the solution; with cold permanganate, instant reduction; with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate, an immediate cherry-red colour. When the base is dissolved in an excess of hydrochloric acid and mixed with sodium nitrite, a yellow solution is obtained which yields with a solution of  $\beta$ -naphthol in aqueous sodium hydroxide a sparingly soluble purple dye. On the addition of sodium hydroxide to a solution containing 2-amino-4-*p*-aminophenylglyoxaline hydrochloride and sodium nitroprusside, a green coloration changing to chestnut-brown is produced.

On the addition of dilute sulphuric acid to an aqueous solution of the base or its hydrochloride, the very sparingly soluble sulphate crystallises in woolly needles.

The *dihydrochloride* crystallises from dilute hydrochloric acid in colourless prisms, which do not melt below  $300^{\circ}$ . It is readily soluble in cold, very readily in hot water.

Found: Cl=28.6; N=22.5.

$C_9H_{10}N_4 \cdot 2HCl$  (247.1) requires Cl=28.7; N=22.7 per cent.

The *dipicrate* forms yellow, silky needles, which darken at  $245^{\circ}$  and decompose at  $250^{\circ}$  (corr.). It is very sparingly soluble even in boiling water.

The benzylidene derivative of 2-amino-4-*p*-aminophenylglyoxaline was not obtained in a crystalline form.

#### *2-Acetylamino-4-p-aminophenylglyoxaline.*

10.6 Grams of 2-amino-4-*p*-aminophenylglyoxaline were boiled with 50 c.c. of acetic anhydride for one hour under a reflux condenser and mixed with aqueous sodium carbonate, when 13.9 grams of the diacetyl derivative were obtained, that is, 98 per cent. of the theoretical yield. The base forms a colourless, crystalline powder which does not melt below  $300^{\circ}$ .

Found: N=21.2.

$C_{13}H_{14}O_2N_4$  (258.2) requires N=21.7 per cent.

It dissolves in dilute hydrochloric acid, but the hydrochloride crystallises almost at once. It appears to be changed by prolonged boiling with hydrochloric acid.

The *hydrochloride* was consequently prepared by triturating the base with an excess of 10 per cent. aqueous hydrochloric acid, draining the insoluble salt, and crystallising it from water, when it

formed colourless, prismatic needles, which did not melt below  $300^{\circ}$ . It is sparingly soluble in cold, fairly readily so in hot water.

Found, in air-dried salt, loss at  $110^{\circ}=11.1$ .

$C_{13}H_{14}O_2N_4 \cdot HCl \cdot 2H_2O$  (330.7) requires  $2H_2O=10.9$  per cent.

Found, in salt dried at  $110^{\circ}$ , C=53.1; H=5.3; N=18.7; Cl=11.6.

$C_{13}H_{14}O_2N_4 \cdot HCl$  (294.7) requires C=53.0; H=5.1; N=19.0; Cl=12.0 per cent.

*Oxidation*.—Ten grams of 2-acetylaminophenylglyoxaline were suspended in 150 c.c. of cold water and mixed with 4 grams of 50 per cent. aqueous sulphuric acid, when a suspension of the sulphate resulted. To this, cold 4 per cent. aqueous potassium permanganate was added until a test portion of the product remained pink for a few seconds, about 240 c.c. being required. The liquor was then filtered from manganese hydroxide, acidified with hydrochloric acid, and extracted with ether. The ethereal extract amounted to 1.5 grams, and after digestion with a little warm water left 1.0 gram of *p*-acetylaminobenzoic acid, which melted at  $260^{\circ}$  (corr.). After recrystallisation from boiling water, the acid formed glistening needles having the same melting point. A specimen of the pure acid from another source and a mixture of the two melted at the same temperature. The identification was confirmed by analysis (Found: C=59.9; H=5.2; N=7.8. Calc.: C=60.3; H=5.1; N=7.8 per cent.) and by hydrolysis to *p*-aminobenzoic acid, which melted at  $190^{\circ}$  (corr.) alone or mixed with the acid resulting from the reduction of *p*-nitrobenzoic acid.

*Reduction of 2-Benzeneazoglyoxaline with Zinc Dust and Acetic Acid: Isolation of Glycoyamidine, Aniline, and 2-Amino-4-p-aminophenylglyoxaline.*

To a boiling solution of 17.2 grams of 2-benzeneazoglyoxaline in 100 c.c. of glacial acetic acid and 300 c.c. of water, 45 grams of zinc dust were added gradually in the course of twenty minutes without further heating. The excess of zinc was removed, the liquor diluted with 2 litres of water, giving an indigo-coloured solution, and treated with hydrogen sulphide. After collecting the zinc sulphide—which had carried down the colouring matter—the liquor was mixed with 20 c.c. of hydrochloric acid and evaporated to dryness. The residue was dissolved in a little water, mixed with sodium carbonate, and extracted with ether, when 2.7 grams of insoluble, black material were deposited; this contained zinc

carbonate and the carbonate of 2-amino-4-*p*-aminophenylglyoxaline. The ethereal extract left on evaporation 7.0 grams of practically pure aniline. The alkaline liquor was acidified faintly with hydrochloric acid, mixed with a solution of 23 grams of picric acid in 1 litre of boiling water, and stirred, when 2.6 grams of 2-amino-4-*p*-aminophenylglyoxaline dipicrate separated immediately as a brownish-yellow, crystalline powder which melted at 240°; for the identification of this substance, the hydrochloride and base were prepared and found to have the properties recorded above.

The filtrate from this salt was kept overnight, when 21.5 grams of a granular, crystalline picrate, melting at 196°, separated, and on concentrating the mother liquor a further 4.8 grams, melting at 180°, were obtained. These crops were mixed, converted into the hydrochloride, and crystallised from alcohol, when eventually 5.9 grams of pure glycoeyamidine hydrochloride were obtained, that is, 43 per cent. of the theoretical yield. It formed clusters of prismatic needles, which began to darken and sinter at 205° and melted at 211–213° (corr.). E. Schmidt (*Arch. Pharm.*, 1913, **251**, 557) states that it begins to discolour at 200° and melts at 208–210° (Found: C=26.5; H=4.4; N=30.6; Cl=26.3.  $C_3H_5ON_3.HCl$  (135.6) requires C=26.6; H=4.5; N=31.0; Cl=26.2 per cent.).

To complete the identification of this compound, the base and some other salts were prepared. The base crystallised from water in colourless, prismatic needles, which began to darken slowly from about 220° and quickly from about 250°, without melting even at 300°. It was anhydrous. (Found: C=36.4; H=4.8; N=42.3.  $C_3H_5ON_3$  (99.1) requires C=36.3; H=5.1; N=42.4 per cent.) E. Schmidt (*loc. cit.*) states that glycoeyamidine darkens from 220°, but does not melt at 250°. It gave with sodium nitroprusside and sodium hydroxide an orange solution, which became Burgundy-red on the addition of acetic acid (Weyl's reaction). It is stable towards cold aqueous permanganate in acid solution, but reduces cold alkaline permanganate, yielding a green solution.

The platinichloride was obtained on spontaneous evaporation of an aqueous solution in large, transparent, quadrilateral tablets having the composition  $C_3H_5ON_3.H_2PtCl_6.2H_2O$ . It begins to darken at 220°, gradually sinters, and is quite black by 260° without actually melting even at 300°. E. Schmidt (*loc. cit.*) found that glycoeyamidine platinichloride had this composition and did not melt at 260°, but sintered and blackened earlier.

The platinichloride was also obtained in an anhydrous form by crystallisation from a hot concentrated solution, when it formed clusters of prisms.

The additive compound with gold chloride,  $C_3H_5ON_3 \cdot AuCl_3$ , melted at  $157-158^\circ$  (corr.). Korndörfer (*Arch. Pharm.*, 1904, **242**, 633) found that glycocyamidine gold chloride had this composition, and melted at  $153-154^\circ$ .

The picrate crystallised from water in glistening, striated, yellow leaflets (flat needles) which melted at  $215-216^\circ$  (corr.). Jaffé (*Zeitsch. physiol. Chem.*, 1906, **48**, 430) describes glycocyamidine picrate as forming needles, which melt at  $210^\circ$ .

## 2- and 4-p-Bromobenzeneazoglyoxaline.

34.4 Grams of *p*-bromoaniline in 200 c.c. of hydrochloric acid and 600 c.c. of water were diazotised at  $-2^\circ$  to  $0^\circ$  by a solution of 14.4 grams of sodium nitrite in 72 c.c. of water. The solution was kept for twenty minutes and poured in a slow stream into a solution of 13.6 grams of glyoxaline and 300 grams of sodium carbonate crystals in 2 litres of water, previously cooled to  $5^\circ$ . After adding a little more aqueous sodium carbonate, the mixture was kept overnight, and the insoluble, yellow powder collected and washed with water. It amounted to 48.7 grams after drying in the air, decomposed at  $245^\circ$ , and was almost completely soluble in dilute hydrochloric acid. After fractional crystallisation from alcohol, there were obtained 37.5 grams of pure 2-*p*-bromobenzeneazoglyoxaline and 5.1 grams scarcely less pure, whilst the final mother liquors deposited a mixture of this compound with dark brown warts, which were separated mechanically, and amounted to about 2.5 grams, melting at about  $175^\circ$ . These were dissolved in dilute hydrochloric acid, and the solution was filtered from a little dark brown, insoluble matter and mixed with ammonia, when a yellow, gelatinous precipitate was formed, which readily became crystalline on warming and stirring. This base was collected and crystallised several times from alcohol, when 4-*p*-bromobenzeneazoglyoxaline was obtained in a pure state.

2-*p*-Bromobenzeneazoglyoxaline crystallises from alcohol in chestnut-brown, prismatic needles, which melt and decompose at  $253^\circ$  (corr.).

Found: C=42.9; H=3.1; N=22.1.

$C_9H_7N_4Br$  (251.1) requires C=43.0; H=2.8; N=22.3 per cent.

4-*p*-Bromobenzeneazoglyoxaline crystallises from alcohol in clusters of brownish-yellow prisms which melt and decompose at  $191^\circ$  (corr.).

Found: C=43.2; H=3.1; N=21.9.

$C_9H_7N_4Br$  (251.1) requires C=43.0; H=2.8; N=22.3 per cent.

On reducing this base (0.26 gram) with stannous chloride and distilling the resulting solution with an excess of sodium hydroxide, the volatile products consisted of *p*-bromoaniline (0.18 gram) and ammonia, which gave 0.05 gram of ammonium chloride.

*Reduction of 2-p-Bromobenzeneazoglyoxaline with Stannous Chloride: Isolation of 2-Aminoglyoxaline, p-Bromoaniline, Guanidine, 2-Amino-4-p-aminophenylglyoxaline, and a Base  $C_9H_9N_4Br$ .*

To 78 grams of 2-*p*-bromobenzeneazoglyoxaline suspended in 40 c.c. of hydrochloric acid and 1 litre of boiling water, 400 c.c. of stannous chloride solution were added. The solution immediately became decolorised, and, after the removal of 0.5 gram of brown, insoluble matter, was concentrated under diminished pressure. The tin salts which separated were collected from time to time and combined, so that the product was obtained in two fractions, consisting of the crystalline tin salts and the syrupy residue.

The crystalline tin salts were dissolved in water and deprived of tin by hydrogen sulphide. The solution of hydrochlorides was evaporated to dryness, dissolved in a little water, and mixed with aqueous sodium carbonate, when 39.6 grams of *p*-bromoaniline separated. The filtrate from this gave a further 1.1 grams of the same compound on extraction with ether, and was next acidified with hydrochloric acid, evaporated to dryness, and extracted with absolute alcohol. (Insoluble material = A.) On distilling the alcohol, a brown syrup remained, which quickly crystallised and became a rock-like mass of 2-aminoglyoxaline hydrochloride, amounting to 15.8 grams and melting at 135–140°.

The syrupy tin salts were also dissolved in water and deprived of tin. The resulting solution was evaporated to dryness, dissolved in a little water, mixed with sodium carbonate, and extracted with ether. This, on concentration, deposited 0.9 gram of colourless needles, melting at 178° (corr.), which proved to be a base having the composition  $C_9H_9N_4Br$  (compare p. 245). The ethereal mother liquor on evaporation left 2.5 grams of dark brown syrup which gradually crystallised, and consisted largely of *p*-bromoaniline.

The alkaline liquor was acidified with hydrochloric acid, evaporated to dryness under diminished pressure, and extracted with absolute alcohol. The insoluble salts, consisting mainly of sodium chloride, were combined with those obtained previously (A), dissolved in water, and mixed with aqueous picric acid, when 2.7 grams of 2-amino-4-*p*-aminophenylglyoxaline dipicrate, melt-

ing at  $240^{\circ}$ , separated; the identity of this salt was confirmed by its conversion into the hydrochloride and base. The alcoholic extract was evaporated under diminished pressure, and left 13.0 grams of brown syrup, which crystallised only partly on seeding with 2-aminoglyoxaline hydrochloride. It was converted into the stannichloride and crystallised fractionally from 10 per cent. hydrochloric acid, when 10.2 grams of 2-aminoglyoxaline stannichloride melting at  $280^{\circ}$  (corr.) were obtained. This is equivalent to 4.9 grams of 2-aminoglyoxaline hydrochloride, the total yield of which was therefore 20.7 grams, that is, 56 per cent. of the theoretical.

The remaining stannichlorides were not readily purified by fractional crystallisation, and were reconverted into hydrochlorides, which amounted to about 3 grams. This material was mixed with sodium carbonate, evaporated until nearly dry, and extracted with hot alcohol.\* The extract was distilled and the residue mixed with an excess of 10 per cent. aqueous oxalic acid, when 1.6 grams of guanidine hydrogen oxalate separated in large crystals. After recrystallisation from water, this salt formed colourless spears, which melted at  $173\text{--}174^{\circ}$  (corr.) after drying at  $100^{\circ}$ , and was sparingly soluble in water.

It had the composition  $\text{CH}_5\text{N}_3\text{C}_3\text{H}_2\text{O}_4\cdot\text{H}_2\text{O}$  previously recorded by Strecker (*Annalen*, 1861, **118**, 160). (Found:  $\text{H}_2\text{O}=10.3$ . Calc.:  $\text{H}_2\text{O}=10.8$ . Found, in dried salt, C=24.0; H=4.9; N=28.0. Calc.: C=24.1; H=4.7; N=28.2 per cent.) The melting point of a specimen of guanidine hydrogen oxalate prepared synthetically and that of a mixture of the two preparations was the same. The identification was confirmed by the preparation of the nitrate and picrate, which had the properties previously recorded.

The base, melting at  $178^{\circ}$  (corr.), obtained as a by-product in the above reaction (compare p. 244), forms colourless needles from alcohol or ether. It contains halogen. It is sparingly soluble in water, readily so in cold, and very easily soluble in hot alcohol, but sparingly so in ether. Its alcoholic solution gradually becomes purple when exposed to the air.

Found: C=43.0; H=3.9; N=21.9.

$\text{C}_3\text{H}_5\text{N}_4\text{Br}$  (253.1) requires C=42.7; H=3.6; N=22.1 per cent.

0.122 Gram mixed with an excess of hydrochloric acid and evaporated to dryness gave 0.153 gram of salt, which is therefore

\* The method employed for the extraction of guanidine carbonate is unsuitable, and it is probable that a considerable proportion remained behind with the sodium carbonate.

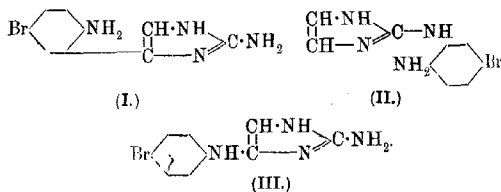


a *dihydrochloride* (calc. yield, 0.157 gram). This salt crystallised from water in elongated leaflets, which, after drying at 100°, melted and decomposed at 245° (corr.) after sintering earlier. The (*di*)*picrate* crystallises from water in woolly needles, which melt at 225° (corr.), and are sparingly soluble in hot, very sparingly so in cold water.

The base decolorises potassium permanganate instantly in cold dilute sulphuric acid solution, and gives a Burgundy-red coloration with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate. When dissolved in dilute hydrochloric acid and mixed with sodium nitrite, it yields a colourless, crystalline precipitate, but the product—crystals and mother liquor—when poured into alkaline  $\beta$ -naphthol gives no coloration.

When an aqueous solution of the hydrochloride is mixed with sodium acetate and benzaldehyde, a turbid, yellow solution is produced—evidently owing to the formation of a benzylidene compound.

The composition and mode of formation of the base indicate that it is 2-*p*-bromobenzenehydrazoglyoxaline, or a substance resulting from this by the benzidine or semidine change. The formation of a dihydrochloride and a benzylidene derivative rule out the first suggestion, whilst the formation of the latter compound also eliminates the semidine-type formula III given below. This formula and the benzidine-type formula I are also incompatible with the behaviour of the compound on treatment with nitrous acid and sodium  $\beta$ -naphthoxide, but the semidine-type formula II, representing 2-5'-*bromo-2'-aminoanilino*glyoxaline, admits the possibility of *o*-diazimine formation with nitrous acid, and is in harmony with all the observed properties of the compound (compare p. 223).



*2-Aminoglyoxaline* (XII, p. 223).

For the purification of 2-aminoglyoxaline, crystallisation of the stannichloride and hydrogen oxalate has proved to be useful.

The free base can be obtained (1) from the hydrochloride by the

addition of an equivalent quantity of sodium carbonate, evaporation to dryness, and extraction with alcohol, and (2) from the hydrogen oxalate by treatment with aqueous barium hydroxide, removal of the excess of this by carbon dioxide, and evaporation of the solution under diminished pressure. In either case, it is obtained as a nearly colourless syrup which gradually turns brown on keeping. It is miscible with water and alcohol, sparingly soluble in chloroform, but hardly soluble in ether or benzene.

The *hydrochloride* crystallises from absolute alcohol in long, colourless plates which melt at  $152^{\circ}$  (corr.). It is deliquescent, and readily soluble in cold, very readily so in hot absolute alcohol. Its aqueous solution reacts neutral to litmus.

Found: C=30.2; H=5.2; N=34.7; Cl=29.9.

$C_3H_5N_3 \cdot HCl$  (119.5) requires C=30.1; H=5.1; N=35.1; Cl=29.7 per cent.

The *stannichloride* crystallises from two to two and a-half times its weight of 10 per cent. hydrochloric acid in prismatic needles, which are anhydrous and melt at  $236^{\circ}$  (corr.). It is readily soluble in water.

Found: Cl=42.4.

$(C_3H_5N_3)_2 \cdot H_2SnCl_6$  (499.6) requires Cl=42.6 per cent.

The *nitrate* separates from water in large, transparent tablets, which are anhydrous, and, after drying at  $100^{\circ}$ , sinter from about  $125^{\circ}$  and melt at  $135-136^{\circ}$  (corr.).

Found: N=38.2.

$C_3H_5N_3 \cdot HNO_3$  (146.1) requires N=38.4 per cent.

The *hydrogen oxalate* crystallises from water in large, colourless tablets, which are anhydrous and melt and effervesce at  $211^{\circ}$  (corr.). It is sparingly soluble in cold, readily so in hot water.

Found: N=24.0.

$C_3H_5N_3 \cdot C_2H_2O_4$  (173.1) requires N=24.3 per cent.

The *picrate* separates from water in long, glistening, silky needles, or in short, prismatic needles, both melting at  $236^{\circ}$  (corr.) after drying at  $100^{\circ}$ . It is sparingly soluble in cold, fairly readily so in hot water.

*Reactions of 2-Aminoglyoxaline.*—2-Aminoglyoxaline hydrochloride dissolved in dilute aqueous copper sulphate gives on the addition of sodium hydroxide a green precipitate, which rapidly darkens and becomes purple-brown. The same precipitate—evidently a copper salt—is obtained eventually with Fehling's solution; no reduction of this solution takes place even on boiling. 2-Aminoglyoxaline nitrate in aqueous silver nitrate gives a white

precipitate on the addition of ammonia; this precipitate is soluble in excess of ammonia, and the solution deposits metallic silver on heating.

2-Aminoglyoxaline hydrochloride in aqueous solution decolorises aqueous potassium permanganate instantly; with ferric chloride, it gives no coloration. With sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate, it gives a deep red colour. On the addition of sodium nitrite to aqueous 2-aminoglyoxaline hydrochloride, a clear, yellow solution is produced which gives a soluble, brownish cherry-coloured dye with  $\beta$ -naphthol in aqueous sodium hydroxide. An aqueous solution of 2-aminoglyoxaline hydrochloride mixed with dilute aqueous sodium nitroprusside gives, on the addition of sodium hydroxide, a deep blue colour, which slowly changes to a bright chestnut on keeping.

2-Aminoglyoxaline is very stable towards hot acids and alkalis. When boiled with 10 per cent. aqueous sodium hydroxide, no ammonia is evolved, and it can be recovered unchanged from the solution. It can be recovered mainly unchanged after heating with concentrated hydrochloric acid for three hours at 170°, and even after three hours at 200° a small proportion can be recovered, together with ammonium chloride and other unidentified products.

An aqueous solution of 2-aminoglyoxaline hydrochloride containing an excess of sodium acetate gives no coloration or other evidence of the formation of a benzylidene derivative when mixed with benzaldehyde.

2-Acetylaminoglyoxaline was prepared by boiling 2-aminoglyoxaline hydrochloride with anhydrous sodium acetate and acetic anhydride for one hour, and mixing the product with aqueous sodium carbonate. It crystallises from water in small prisms which melt to a brown liquid at 287° (corr.), after sintering and darkening from about 270°. It is anhydrous and sparingly soluble in cold water, but fairly readily so in hot water.

Found: C=47.7; H=5.7; N=33.4.

$C_5H_7ON_3$  (125.1) requires C=48.0; H=5.6; N=33.6 per cent.

The reactions of this substance are described with those of the next compound.

2-Benzoylaminoglyoxaline was prepared by the Schotten-Baumann method. The crude product collected from the reaction liquor appears to be a di- or tri-benzoylaminoglyoxaline. After washing with ether to remove benzoic anhydride, it formed a nearly colourless, crystalline powder, which contained only a trace of chloride, but gave an odour of benzoyl chloride when boiled with dilute hydrochloric acid. When treated with a little hot alcohol,

it dissolved, and 2-benzoylaminoglyoxaline crystallised from the hot liquor, whilst the mother liquor from this left an oil—apparently ethyl benzoate—on distillation. 2-Benzoylaminoglyoxaline was purified by crystallisation from alcohol, from which it separates in glistening leaflets, melting at 227° (corr.) after sintering earlier. It is sparingly soluble even in hot alcohol, and almost insoluble in boiling water.

Found: C=63.9; H=4.9; N=22.4.

$C_{10}H_9ON_3$  (187.1) requires C=64.1; H=4.9; N=22.5 per cent.

2-Acetylaminoglyoxaline and 2-benzoylaminoglyoxaline are soluble in dilute hydrochloric acid and in aqueous sodium hydroxide, but not in aqueous sodium carbonate. They give cherry-red solutions with sodium diazobenzene-*p*-sulphonate in sodium carbonate, but do not give colorations with sodium nitroprusside and sodium hydroxide. They do not change the colour of cold aqueous acid permanganate, but give green solutions with cold aqueous permanganate in sodium hydroxide solution. When mixed with hydrochloric acid and sodium nitrite, they do not couple with  $\beta$ -naphthol in aqueous sodium hydroxide.

#### *The Benzeneazo-4-methylglyoxalines.*

37.2 Grams of aniline in 100 c.c. of hydrochloric acid and 300 c.c. of water were diazotised with 28.8 grams of sodium nitrite in 150 c.c. of water. The solution was run slowly into a solution of 32.5 grams of 4-methylglyoxaline and 100 grams of sodium hydrogen carbonate in 2 litres of water at 10° and kept overnight. The orange precipitate was collected, washed well with water (filtrate *F*), and triturated successively with 500, 250, and 250 c.c. of 2.5 per cent. aqueous hydrochloric acid. The insoluble fraction formed a dark red powder, which amounted to 23.2 grams, and decomposed at 175° after sintering from 160°. On crystallisation from 300 c.c. of alcohol, it gave 17.3 grams of pure 2:5-bisbenzeneazo-4-methylglyoxaline, the remainder of the material forming a black resin.

The hydrochloric acid extract was basified with sodium carbonate, and gave 40.4 grams of a yellow, crystalline powder, which sintered from 160° and decomposed at 195°. On crystallisation from 400 c.c. of alcohol, it gave, successively, 13.1 grams melting at 235°, 3.9 grams melting at 232°, which both gave 5-benzeneazo-4-methylglyoxaline on recrystallisation, then 7.4 grams melting at 175°, which gave 2-benzeneazo-4-methylglyoxaline on recrystallisation, then 12.4 grams of a mixture of the two compounds.

Owing to the formation of the bis-compound in the above reaction, the benzenediazonium chloride employed was insufficient to combine with the whole of the methylglyoxaline present, and it was calculated that 10.5 grams of this remained in the filtrate *F*. This was accordingly treated with a diazo-solution prepared from 11.3 grams of aniline, and gave further quantities of the substances described above, 5.3 grams of the bis-compound and 5.6 grams of 5-benzeneazo-4-methylglyoxaline being obtained in a nearly pure state.

2-Benzeneazo-4-methylglyoxaline (XIV, p. 224) crystallises from alcohol in orange prisms, which melt at 185° (corr.).

Found: C=64.8; H=5.6; N=30.1.

$C_{10}H_{10}N_4$  (185.2) requires C=64.5; H=5.4; N=30.1 per cent.

5-Benzeneazo-4-methylglyoxaline (XVIII, p. 224) crystallises from alcohol in flat, glistening, copper-coloured needles, which melt and decompose at 240° (corr.).

Found: C=64.5; H=5.6; N=30.0.

$C_{10}H_{10}N_4$  (185.2) requires C=64.5; H=5.4; N=30.1 per cent.

2:5-Bisbenzeneazo-4-methylglyoxaline separates from alcohol in prismatic needles and from ethyl acetate in cubes. Both forms are garnet-red in colour and melt and decompose at 206° (corr.).

Found: C=66.0, 65.9; H=5.1, 5.1; N=28.8, 28.8.

$C_{16}H_{14}N_6$  (290.2) requires C=66.2; H=4.9; N=29.0 per cent.

This substance is readily soluble in alcohol, ethyl acetate, or acetone, fairly readily so in chloroform, but sparingly so in ether or benzene.

It is soluble in aqueous sodium hydroxide, and is reprecipitated unchanged on the addition of acetic acid. It is only very sparingly soluble in dilute hydrochloric acid. When boiled with 10 per cent. aqueous hydrochloric acid, it is quickly resinified with effervescence, doubtless due to nitrogen, and the production of an odour of phenol.

#### *Reduction of 2-Benzeneazo-4-methylglyoxaline with Stannous Chloride.*

1.5 Grams of 2-benzeneazo-4-methylglyoxaline gave 1.4 grams of 2-amino-5-*p*-aminophenyl-4-methylglyoxaline dihydrochloride when reduced with stannous chloride in the manner previously described for the lower homologue (p. 238).

2-Amino-5-*p*-aminophenyl-4-methylglyoxaline dihydrochloride crystallises from water in diamond-shaped plates, which are anhydrous and do not melt below 300°. It is readily soluble in cold, very readily so in hot water.

Found: C=46.0, 45.9; H=5.5, 5.5.

$C_{10}H_{12}N_4 \cdot 2HCl$  (201.0) requires C=46.0; H=5.4 per cent.

When boiled with an excess of aqueous sodium carbonate and animal charcoal, it yields the *monohydrochloride*, unlike the lower homologue, which yields the corresponding base under this treatment.

The *monohydrochloride* crystallises from alcohol in flat needles which sinter at about  $80^\circ$ , become discoloured rapidly about  $240^\circ$ , and melt at  $260^\circ$  (corr.). It is readily soluble in hot water or alcohol, less so in these solvents when cold.

Found, in air-dried base, loss at  $60^\circ$  in a vacuum, 13.2, 13.3.

$C_{10}H_{12}N_4 \cdot HCl \cdot 2\frac{1}{2}H_2O$  requires loss of  $2H_2O=13.4$  per cent.

Found, in base so dried: C=51.5; H=5.6; N=24.0, 24.0;  
Cl=14.9.

$C_{10}H_{12}N_4 \cdot HCl \cdot \frac{1}{2}H_2O$  (233.7) requires C=51.4; H=6.0; N=24.0;  
Cl=15.2 per cent.

The *dipicrate* forms glistening, yellow needles, which melt and decompose at  $255^\circ$  (corr.) after darkening earlier. It is very sparingly soluble even in boiling water.

An aqueous solution of the hydrochloride reduces cold ammoniacal silver nitrate. It gives, with Fehling's solution, a greyish-green precipitate, which becomes pale brown on boiling the liquor; with cold aqueous acid permanganate, instant reduction; with sodium diazobenzene-*p*-sulphonate, a pale orange colour, which deepens on keeping; with hydrochloric acid and sodium nitrite, an orange-yellow solution, which yields a sparingly soluble claret dye when added to a solution of  $\beta$ -naphthol in aqueous sodium hydroxide. On the addition of sodium hydroxide to an aqueous solution of the hydrochloride and sodium nitroprusside, an orange colour is produced, which changes to green on the addition of acetic acid.

The *diacetyl* derivative was prepared by the action of sodium acetate and acetic anhydride on the dihydrochloride, and was purified by crystallisation of the hydrochloride.

*2-Acetyl-amino-5-p-acetylaminophenyl-4-methylglyoxaline hydrochloride* crystallises from water in felted, silky needles, which are sparingly soluble in cold water, contain  $4H_2O$ , and, after drying at  $100^\circ$ , melt and decompose at  $303^\circ$  (corr.).

Found, in air-dried salt, loss at  $100^\circ=19.0$ .

$C_{14}H_{16}O_2N_4 \cdot HCl \cdot 4H_2O$  requires  $H_2O=18.9$  per cent

Found, in salt dried at  $100^\circ$ , Cl=11.4.

$C_{14}H_{16}O_2N_4 \cdot HCl$  (308.7) requires Cl=11.5 per cent.

On adding ammonia to an aqueous solution of the hydrochloride, the base was precipitated in minute, glistening needles, which, after drying at  $100^{\circ}$ , melted to a red liquid at  $280^{\circ}$  (corr.).

*Monobenzylidene Derivative.*—To 0.5 gram of the dihydrochloride in 5 c.c. of water there were added, first, 0.55 gram of sodium acetate in 5 c.c. of water, and then 0.5 c.c. of benzaldehyde, and the mixture was stirred. A yellow colour was developed, and the aqueous liquor became turbid and gradually deposited crystals. On adding a few drops of acetic acid and ether, the quantity of crystals was increased. They were collected and washed with water and ether, when there remained 0.5 gram of a pale yellow, crystalline powder, which proved to be the acetate of 2-amino-5-p-benzylideneaminophenyl-4-methylglyoxaline. When dried at  $100^{\circ}$ , it melts and decomposes at  $208^{\circ}$  (corr.), after sintering and darkening earlier.

Found, in substance dried in a vacuum, C=67.2; H=6.2; N=16.2.\*

$C_{17}H_{16}N_4C_2H_4O_2$  (336.3) requires C=67.8; H=6.0; N=16.7 per cent.

This salt is very sparingly soluble in cold water, but slightly in boiling water, with which, however, it gives an odour of benzaldehyde, and thus appears to suffer hydrolysis. When mixed with aqueous sodium carbonate, it yields the base as a deep yellow, in soluble gum, which could not be obtained in crystalline form. When the acetate is moistened with 10 per cent. aqueous hydrochloric acid, it turns red, but does not dissolve until the mixture is warmed, when the red colour disappears.

*Reduction of 2-Benzeneazo-4-methylglyoxaline with Zinc Dust and Acetic Acid.*

Two grams of the azo-compound were reduced by the method applied to the lower homologue (p. 241) and worked up in the same manner as far as the removal of the aniline by extraction with ether. The solvent removed 0.65 gram of crude aniline. The alkaline liquor remaining was acidified with hydrochloric acid, evaporated to dryness, and extracted with absolute alcohol, when 1.4 grams of brown syrup were removed. This, when dissolved in a little absolute alcohol and kept, deposited 0.7 gram of nearly pure alacreatinine hydrochloride.

This was converted into the picrate, when a very small quantity of 2-amino-5-p-aminophenyl-4-methylglyoxaline dipicrate separated

\* The substance left a trace of ash on combustion.

from the hot solution, whilst, on cooling, alacreatinine picrate crystallised out. After recrystallisation, the salt was obtained in a pure state, and was converted into the base and hydrochloride by the usual methods.

Alacreatinine crystallises from water in stout, elongated prisms which resemble carbamide, and contain  $1\text{H}_2\text{O}$ , as previously stated by Baumann (*Annalen*, 1873, **167**, 83). After drying at  $100^\circ$ , it melts at  $222\text{--}223^\circ$  (corr.). (Found, in air-dried salt,  $\text{H}_2\text{O}=13.6$ . Calc.: 13.7. Found, in dried salt,  $\text{C}=42.4$ ;  $\text{H}=6.3$ ;  $\text{N}=36.9$ . Calc.:  $\text{C}=42.5$ ;  $\text{H}=6.2$ ;  $\text{N}=37.1$  per cent.)

It does not give Weyl's reaction, and does not reduce cold aqueous acid permanganate, but gives a green solution with cold alkaline permanganate.

The *hydrochloride* crystallises from absolute alcohol in clusters of prisms, which are anhydrous and melt at  $202\text{--}203^\circ$  (corr.). It is very readily soluble in water, sparingly soluble in cold, fairly readily so in hot alcohol.

Found:  $\text{Cl}=23.6$ .

$\text{C}_4\text{H}_7\text{ON}_3, \text{HCl}$  (149.6) requires  $\text{Cl}=23.7$  per cent.

The *picrate* separates from water in yellow, prismatic needles, which are anhydrous and melt and decompose at  $212^\circ$  (corr.) after sintering from about  $200^\circ$ . It is sparingly soluble in cold, fairly readily so in hot water.

Found:  $\text{N}=24.5$ .

$\text{C}_4\text{H}_7\text{ON}_3, \text{C}_6\text{H}_3\text{O}_7\text{N}_3$  (342.2) requires  $\text{N}=24.6$  per cent.

#### *Reduction of 5-Benzeneazo-4-methylglyoxaline with Stannous Chloride.*

Fourteen grams of the azo-compound were dissolved in a boiling mixture of 70 c.c. of 10 per cent. aqueous hydrochloric acid and 140 c.c. of water, and mixed with 80 c.c. of stannous chloride solution. The crystalline and residual tin salts were separated as in the experiments described earlier, and decomposed separately by hydrogen sulphide. The crystalline salts gave a solution of hydrochlorides, which, when evaporated nearly to dryness and mixed with alcohol, left 6.1 grams of ammonium chloride undissolved. (Alcoholic mother liquor = A.) The residual salts gave a solution of hydrochlorides, which on concentration deposited 1.7 + 0.5 grams of the *hydrochloride*,  $\text{C}_9\text{H}_{10}\text{ON}_2, \text{HCl}$ , described below, and on further concentration and addition of alcohol gave 1.5 grams of ammonium chloride. The alcoholic mother liquor was combined



with *A*, and gave 4.7 grams of aniline, together with 3.8 grams of a brown, gummy, hydrochloride. This was a mixture from which only very small quantities of crystalline compounds were isolated by various methods of treatment.

The *hydrochloride*,  $C_9H_{10}ON_2.HCl$ , crystallises from water in colourless, transparent, rectangular tablets, which melt and effervesce at  $308^\circ$  (corr.) after sintering and darkening earlier. It is readily soluble in hot, less so in cold water, giving a solution which is strongly acid to litmus.

Found, in air-dried salt, loss at  $110^\circ = 1.7$ .

Found, in salt dried at  $110^\circ$ : C=54.8, 54.8, 55.0; H=5.9, 5.0, 5.2; N=13.5; Cl=17.2.

$C_9H_{10}ON_2.HCl$  (198.6) requires C=54.4; H=5.6; N=14.1; Cl=17.8 per cent.

The corresponding *base* is obtained by adding ammonia to a concentrated aqueous solution of the hydrochloride. It crystallises from water in brilliant, elongated prisms, which are anhydrous and melt at  $185^\circ$  (corr.).

Found: C=66.6, 66.1; H=6.2, 6.1; N=17.8, 17.2.

$C_9H_{10}ON_2$  (162.1) requires C=66.6; H=6.2; N=17.3 per cent.

The base is more readily soluble in dilute aqueous sodium hydroxide than in water. With silver nitrate it yields a white precipitate, which dissolves on the addition of ammonia; on boiling this solution, no reduction takes place. The base does not reduce Fehling's solution on boiling.

It is stable towards cold aqueous acid potassium permanganate, but slowly reduces cold alkaline permanganate, giving a green solution. It gives no coloration with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate. When dissolved in hydrochloric acid and mixed with sodium nitrite, it fails to couple with  $\beta$ -naphthol in aqueous sodium hydroxide. The hydrochloride is recovered slightly charred, but otherwise unchanged, after the action of concentrated hydrochloric acid at  $170^\circ$  for two and a-half hours.

The quantity of this compound available was insufficient for the determination of its constitution, and we are consequently unable to offer any suggestion as to how one of the carbon atoms of the starting material has been eliminated. It is perhaps worth recording that the formula  $C_9H_{10}ON_2$  is that of a phenyldihydroglyoxalone.

*Reduction of 5-Benzeneazo-4-methylglyoxaline with Zinc Dust and Acetic Acid.*

Ten grams of the azo-compound were dissolved in 150 c.c. of boiling 50 per cent. acetic acid and reduced by adding gradually 16 grams of zinc dust. After removing the zinc as sulphide, the liquor was mixed with 20 c.c. of hydrochloric acid, evaporated to a syrup, and mixed with alcohol, when 1.3 grams of ammonium chloride were collected. The alcoholic mother liquor was deprived of the solvent, dissolved in water, mixed with sodium carbonate, and shaken with ether, when 1.6 grams of the base,  $C_{10}H_{11}ON_3$ , described below, separated as a nearly colourless, insoluble, crystalline powder. The ethereal solution left on evaporation 3.3 grams of aniline. From the alkaline liquor, 5.5 grams of a mauve varnish were obtained, from which only small quantities of crystalline substances could be isolated by various methods of treatment.

The base,  $C_{10}H_{11}ON_3$ , crystallises from water in small, colourless, glistening, rhomboidal plates, which are anhydrous and melt at  $265^\circ$  (corr.). It is very sparingly soluble in cold water, rather more readily in boiling water.

Found: C = 63.7; H = 6.2; N = 22.0.

$C_{10}H_{11}ON_3$  (189.2) requires C = 63.5; H = 5.9; N = 22.2 per cent.

The hydrochloride crystallises from absolute alcohol in transparent, oblong plates which melt at  $206-208^\circ$  (corr.). It is readily soluble in water, concentrated hydrochloric acid, or hot alcohol. Its aqueous solution reacts strongly acid to litmus.

The base dissolves slowly in cold 10 per cent. aqueous sodium hydroxide, readily on warming, and a well-crystallised sodium salt separates from the solution in prismatic needles. This salt is decomposed by carbon dioxide with the regeneration of the base. A solution of the base in aqueous sodium hydroxide gives with Fehling's solution no change in the cold, but a green precipitate on boiling. A solution of the base in nitric acid gives no precipitate with silver nitrate, but on the addition of ammonia a white precipitate, which dissolves on heating the solution, reappears on cooling, and is soluble in excess of ammonia. An aqueous solution of potassium permanganate is unaffected by a solution of the base in sulphuric acid, but turns green with a solution of the base in aqueous sodium hydroxide. The base does not couple with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate, and when dissolved in hydrochloric acid and mixed with sodium nitrite does not couple with sodium  $\beta$ -naphthoxide.

When the hydrochloride is heated with concentrated hydrochloric

acid for two and a-half hours at  $170^{\circ}$ , it is decomposed, with the formation of ammonium chloride and a hydrochloride, which crystallises from alcohol in plates, melting and decomposing at about  $280^{\circ}$  (corr.).

*4-Benzeneazo-2-methylglyoxaline.*

This was prepared by the action of benzenediazonium chloride on 2-methylglyoxaline in aqueous sodium carbonate. The crude product readily resinified when boiled with alcohol, and only a small proportion was obtained in a pure state. It forms brick-red prisms, which melt at  $158^{\circ}$  (corr.) and are very readily soluble in alcohol.

Found: C=64.3; H=5.7; N=30.0.

$C_{10}H_{10}N_4$  (186.2) requires C=64.5; H=5.4; N=30.1 per cent.

*4-p-Bromobenzeneazo-2-methylglyoxaline.*

This was prepared in good yield by the action of *p*-bromobenzenediazonium chloride on 2-methylglyoxaline in aqueous sodium carbonate. It crystallises from absolute alcohol in red, rhomboidal prisms, which are anhydrous and melt and decompose at  $200^{\circ}$  (corr.).

Found: N=21.0.

$C_{10}H_9N_4Br$  (265.1) requires N=21.1 per cent.

From ordinary alcohol, it separates in elongated prisms, which lose 2.2 per cent. of water at  $60^{\circ}$  in a vacuum. This hydrated form melts at about  $135^{\circ}$  when heated quickly, and softens at this temperature when heated slowly, finally melting at about  $190^{\circ}$ . It can be dehydrated by crystallisation from absolute alcohol.

The reduction of this compound with either stannous chloride or zinc dust and acetic acid led to mixtures of products, from which no crystalline compounds except *p*-bromoaniline and ammonium chloride could be isolated.

*2-Phenyl-4-p-bromobenzeneazoglyoxaline.*

8.6 Grams of *p*-bromoaniline were diazotised and the liquor added to 7.2 grams of 2-phenylglyoxaline and 70 grams of hydrated sodium carbonate in 4 litres of water at  $8^{\circ}$ , the solution being vigorously stirred during the addition. Separation of an orange

precipitate began at once, but was not complete until forty-eight hours had elapsed. The crude product was crystallised from alcohol, and gave 13 grams of the pure azo-compound.

2-Phenyl-4-p-bromobenzenediazoglyoxaline crystallises from alcohol in clusters of fine, orange needles, which melt at  $201^{\circ}$  (corr.), and are anhydrous.

Found: N=16.9.

$C_{13}H_{11}N_4Br$  (327.1) requires N=17.1 per cent.

*Reduction of 2-Phenyl-4-p-bromobenzenediazoglyoxaline with Stannous Chloride: Formation of a Base,  $C_{13}H_{13}N_4Br$ .*

Two grains of the azo-compound were suspended in 20 c.c. of boiling 5 per cent. aqueous hydrochloric acid and mixed with 10 c.c. of stannous chloride solution. The solution was filtered quickly from a little resinous matter and mixed with 20 c.c. of concentrated hydrochloric acid, when a crystalline tin salt separated. This was deprived of tin, and the filtrate was evaporated to a small volume, when 0.85 gram of a crystalline hydrochloride separated.

This hydrochloride crystallises from dilute hydrochloric acid in nearly colourless needles, which, after drying in a vacuum, melt and decompose at  $255^{\circ}$  (corr.).

Found: C=45.0; H=3.8; N=13.7.

$C_{13}H_{13}N_4Br \cdot 2HCl$  (402.0) requires C=44.8; H=3.8; N=13.9 per cent.

0.1530 gave, by Carius's method, 0.1750 AgCl + AgBr. Calc., 0.1806.

It is sparingly soluble in cold water, more readily so in hot water. The aqueous solution gradually acquires a purple colour in the air or on the addition of acidified aqueous potassium permanganate. In the presence of an excess of hydrochloric acid, aqueous solutions are stable in the air. Sodium carbonate or ammonia precipitate the base as a grey, flocculent precipitate which is soluble in ether, the ethereal solution rapidly assuming a purple colour. On the addition of sodium hydroxide to an aqueous solution of the hydrochloride, a pale purple solution results. On adding sodium diazobenzene-*p*-sulphonate to a dilute solution of the compound in the presence of sodium carbonate, a dull purple colour is produced. An aqueous solution of the hydrochloride containing an excess of hydrochloric acid gives on the addition of

sodium nitrite a deep orange solution, which yields a sparingly soluble purple dye with sodium  $\beta$ -naphthoxide. On mixing a solution of the hydrochloride in dilute acetic acid with sodium acetate and benzaldehyde, there is evidence of the formation of a benzylidene derivative. When an aqueous solution of the hydrochloride is mixed with sodium nitroprusside, a pale buff precipitate is formed, which dissolves in sodium hydroxide, giving a deep red solution.

The *triacetyl* derivative was obtained by heating the hydrochloride for one hour on the water-bath with an excess of acetic anhydride and anhydrous sodium acetate. On heating the product with aqueous sodium carbonate, it separated as a slate-grey, crystalline powder, which did not melt at  $300^{\circ}$ .

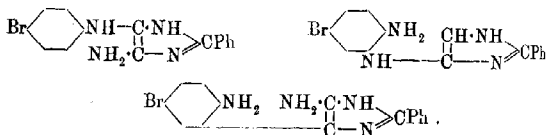
Found: C=55.2; H=4.1; N=12.6, 12.7; Br=17.3.

$C_{21}H_{19}O_3N_4Br$  (455.2) requires C=55.4; H=4.2; N=12.3;

Br=17.6 per cent.

It is almost insoluble in boiling water or alcohol, and does not dissolve in dilute acids or in aqueous sodium hydroxide.

From its mode of formation, composition, and properties, it is clear that the hydrochloride,  $C_{15}H_{13}N_4Br \cdot 2HCl$ , arises from 2-phenyl-4-*p*-bromobenzenehydrazoglyoxaline by a change of the semidine or benzidine type, but it is not possible to decide definitely without further evidence which of the three formulæ given below represents its constitution.



*2-p-Sulphobenzeneglyoxaline-4:5-dicarboxylic Acid*  
(XX, p. 226).

20.8 Grams of sulphanilic acid were converted into diazobenzene-*p*-sulphonic acid, and the moist crystals (representing about 20 grams of dry substance) were added to a cold solution of 16 grams of glyoxaline-4:5-dicarboxylic acid in 240 c.c. of 10 per cent. aqueous sodium hydroxide. After keeping for one and a-half hours, the liquor was mixed with sufficient glacial acetic acid (36 c.c.) to neutralise the alkali, cooled, and kept for half an hour, when a mass of silky, yellow needles—the disodium salt of the new

acid, separated. These were recrystallised twice from 200 c.c. of water, and finally dissolved in 150 c.c. of hot water and mixed with 50 c.c. of hydrochloric acid, when 12 grams of 2-*p*-sulphobenzene-azoglyoxaline-4:5-dicarboxylic acid separated in red, microscopic prisms mixed with some smaller crystals of glyoxaline-4:5-dicarboxylic acid, from which it was purified by fractional crystallisation from water.

The acid separates from water with  $2\text{H}_2\text{O}$ , which is lost at  $130^\circ$  in a vacuum, but not at  $100\text{--}110^\circ$  under normal pressure.

Found, in air-dried substance, loss at  $130^\circ$  in a vacuum = 10.0;  
 $\text{C} = 35.5$ ;  $\text{H} = 3.3$ ;  $\text{N} = 15.1$ ;  $\text{S} = 8.2$ .

$\text{C}_{11}\text{H}_8\text{O}_7\text{N}_4\text{S}, 2\text{H}_2\text{O}$  (376.2) requires  $\text{H}_2\text{O} = 9.6$ ;  $\text{C} = 35.1$ ;  $\text{H} = 3.3$ ;  
 $\text{N} = 14.9$ ;  $\text{S} = 8.5$  per cent.

It is sparingly soluble in cold water, but readily so in hot. It is soluble in aqueous alkalis, but not more soluble in dilute aqueous mineral acids than in water.

The disodium salt separates in yellow, silky needles, which contain  $3\text{H}_2\text{O}$ , when the acid is dissolved in aqueous sodium hydroxide and sufficient acetic acid is added to combine with the alkali. It is readily soluble in hot water, somewhat sparingly so in cold.

Found, in air-dried salt, loss at  $100^\circ = 11.6$ ,  $12.6$ .

$\text{C}_{11}\text{H}_6\text{O}_7\text{N}_4\text{SNa}_2, 3\text{H}_2\text{O}$  (438.2) requires  $3\text{H}_2\text{O} = 12.3$  per cent.

Found, in salt dried at  $100^\circ$ ,  $\text{S} = 8.2$ ;  $\text{N} = 11.7$ .

$\text{C}_{11}\text{H}_6\text{O}_7\text{N}_4\text{SNa}_2$  (384.2) requires  $\text{S} = 8.4$ ;  $\text{N} = 12.0$  per cent.

*Reduction of 2-p-Sulphobenzene-azoglyoxaline-4:5-dicarboxylic Acid: Formation of 2-Aminoglyoxaline-4:5-dicarboxylic Acid (XXI, p. 226).*

6.2 Grams of the disodium salt were dissolved in 60 c.c. of 10 per cent. aqueous sodium hydroxide, mixed with 12 grams of sodium hyposulphite (80 per cent.), and boiled. The nearly colourless solution was kept overnight, acidified with hydrochloric acid, boiled, and filtered hot, when 1.6 grams of crude 2-aminoglyoxaline-4:5-dicarboxylic acid separated. This was purified by solution in aqueous sodium hydroxide, filtration, and reprecipitation with hydrochloric acid, and finally crystallised from about 500 c.c. of dilute hydrochloric acid.

2-Aminoglyoxaline-4:5-dicarboxylic acid forms minute, pale buff needles, which effervesce at  $245^\circ$  (corr.) and then melt. It is very sparingly soluble in cold water, a little more readily in hot.

Found, in substance dried at  $110^{\circ}$ , C=34.6; H=3.2; N=24.6.  
 $C_8H_5O_4N_3$  (171.1) requires C=35.1; H=3.0; N=24.6 per cent.

It is soluble in aqueous alkalis, but not appreciably more soluble in dilute acids than in water. An aqueous solution, acidified with sulphuric acid, decolorises cold aqueous permanganate instantly. When treated with hydrochloric acid and sodium nitrite and poured into a solution of  $\beta$ -naphthol in aqueous sodium hydroxide, it gives a reddish-brown colour. With sodium diazobenzene- $\mu$ -sulphonate in aqueous sodium carbonate, it gives a reddish-brown colour. It does not give any characteristic colour with sodium nitroprusside and sodium hydroxide.

*Action of Water at  $170^{\circ}$ .*—After a preliminary experiment, in which it was found that the product contained ammonium carbonate, 1.33 grams of the acid and 30 c.c. of water were heated in a sealed tube for twelve hours at  $170^{\circ}$ , when a dark brown deposit formed. After adding alkali and distilling into standard acid, 0.157 gram of ammonia was found, whereas 0.132 gram represents the liberation of one molecular proportion. From the residue of the distillation, small quantities of a crystalline picrate were isolated, but in insufficient amount for characterisation.

*Action of Boiling Aniline.*—0.9 Gram of the acid was boiled with 10 c.c. of aniline for six hours under a reflux condenser, in which a small quantity of ammonium carbonate collected. The product was distilled with steam to remove aniline, and left a pale brown, aqueous liquor containing some resinous matter. The liquor was cooled, filtered, and mixed with cold saturated aqueous picric acid, when 1.0 gram of a crystalline picrate, melting at about  $215^{\circ}$ , was obtained. After crystallising this from water twice, it gave 0.4 gram of 2-aminoglyoxaline picrate, melting at  $234^{\circ}$  (corr.), the pure substance melting at  $236^{\circ}$ , and a mixture of the two at  $234^{\circ}$  in the same bath. From the picrate, the hydrochloride and stannichloride were prepared, and identified as the salts of 2-aminoglyoxaline previously described.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,  
 LONDON, E.C.1.

[Received, February 7th, 1919.]

## Organic Chemistry.

**Products of the Action of the Silent Electric Discharge on Acetylene.** H. P. KAUFMANN (*Annalen*, 1918, 417, 34—59).—

After giving a résumé of previous work on this subject, the author describes in detail his own apparatus, photographs of which are given. The essential part consists of two concentric glass tubes about 75 cm. long having a space of 5 mm. between their walls. The interior of the inner tube is silvered, and through it a rapid stream of cold water is passed. The outer tube is immersed in dilute sulphuric acid, in which is a cooling coil. Electrical connexion is made between the silvered surface and the sulphuric acid with the poles of an induction coil operated by a high-frequency machine (230—250 volts, 2·5—3 amperes). A stream of acetylene is passed between the tubes, and all air in the apparatus must be completely displaced by the acetylene before the silent discharge is passed. When the reaction vessel is allowed to get warm, the product is a mixture of a solid and a liquid, but if the vessel is kept cold, a liquid product only is obtained, which collects at the bottom of the vessel at the rate of about 30—50 grams per hour. The liquid is a brown, viscous oil having an unpleasant odour. It has the composition  $(C_2H_2)_x$  and is very unstable, changing by warming, by keeping in solution, or by the attack of almost any chemical agent into the solid, which appears to be identical with that described by de Wilde (*Ber.*, 1874, 7, 337). The liquid decomposes and carbonises above  $100^\circ$ , but a small quantity distils at  $70^\circ/10$  mm., which is a mixture of several substances; the residue in the flask changes to a plastic mass, which ultimately becomes brittle.

The solid product obtained in the warm reaction vessel is more conveniently obtained by warming a solution of the liquid product in ether at about  $60^\circ$ . It is a pale yellow, odourless powder, which is insoluble in all solvents.

Both the liquid and the solid rapidly absorb oxygen, and it is only during such absorption that they produce any action on a photographic plate.

The solid does not react with a dilute solution of bromine under ordinary conditions, but is attacked by more concentrated solutions, hydrogen bromide being evolved. The liquid readily absorbs bromine, best in solution in carbon tetrachloride, a pale yellow powder being obtained, the composition of which appears to be  $(C_2H_2Br)_x$ , assuming it to be an individual substance.

A 98% alcoholic solution of silver nitrate produces with a solution of the liquid product in carbon tetrachloride a pale yellow, flocculent precipitate of a silver derivative, which explodes on heating; the presence of a  $:CH$  group in the liquid product is thus indicated.

By boiling with 47% nitric acid, the solid product yields nitro-



compounds of high molecular weight, together with a little benzoic acid. By oxidation with alkaline permanganate, the liquid product yields benzoic, *isophthalic*, and *terephthalic* acids. The same three acids are obtained, although with much greater difficulty, by oxidising the solid product with alkaline permanganate. C. S.

**Allyl Alcohol.** M. J. STRITAR (*Monatsh.*, 1918, **39**, 617—626).—Bromine is quantitatively absorbed by allyl alcohol whether the former is in excess or not; the reaction is suitable for the exact quantitative estimation of allyl alcohol, which may be effected either by direct titration with bromine water until a permanent yellow coloration is obtained, or by treating the acidified aqueous solution of the alcohol with an excess of bromide-bromate solution, followed by addition of potassium iodide and titration of the liberated iodine with sodium thiosulphate (compare Stritar and Zeidler, A., 1904, ii, 686).

When bromination is effected in dilute aqueous solution, about 47.5% of the added bromine is immediately and spontaneously eliminated as hydrogen bromide. Elimination of the second bromine atom (exchange for hydroxyl) occurs slowly and incompletely in acid solution, small amounts of acetaldehyde being formed. Practically the whole of the bromine is removed when the product is heated under pressure at 100° with the calculated quantity of potassium hydroxide (or with a 10% excess); the yield of glycerol is about 97% of that theoretically possible. The small deficiency is caused by the formation of a volatile, saturated bromide which is fairly resistant to alkali. H. W.

**The System Ethyl Ether-Chloroform.** A. SMITS and V. S. F. BERCKMANS (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 401—404).—A melting-point curve for various mixtures of ethyl ether and chloroform has been determined. The curve shows that an equimolecular compound is formed (m. p.  $-94.4^{\circ}$ ), as was stated by Dolezalek and Schulze (A., 1913, ii, 108), but, in addition, two other compounds, (i) a compound made up of two molecules of chloroform and one molecule of ethyl ether (m. p.  $-93.3^{\circ}$ ), and (ii) one made up of two molecules of ethyl ether and one of chloroform. The latter compound does not melt, but dissociates at  $-113.8^{\circ}$  into the equimolecular compound and ethyl ether.

J. F. S.

**Physical Constants of "Mustard Gas" [ $\beta\beta$ -Dichloroethyl Sulphide].** LEASON H. ADAMS and ERSKINE D. WILLIAMSON (*J. Washington Acad. Sci.*, 1919, **9**, 30—35).—The compressibility of  $\beta\beta$ -dichloroethyl sulphide has been determined over the pressure range 392—1713 megabars at  $31.5^{\circ}$  by the method previously described (this vol., ii, 98). The compressibility is represented by the equations  $\Delta v/v_0 = 4.24 \times 10^{-5}(P - P_0) - 6.3 \times 10^{-5}(P - P_0)^2$  and  $-\Delta v/v_0 = 0.118(1 - e^{-0.364 \times 10^{-3}P - P_0})$ . Differentiating this, the relationship  $-dv/dP = 49.5e^{-0.364 \times 10^{-3}P}$ . The compressibility at

$P=0$  is  $49.5 \times 10^{-6}$  per megabar, and at 1000 megabars it is  $34.4 \times 10^{-6}$  per megabar. The freezing pressure and volume change were also determined at a few temperatures, and the following results obtained:

Temp.	Freezing pressure.		$dP/dT$ .
	Megabars.	$(V_2 - V_1 \text{ c.c.})$	
13.9	1	0.054	68
21.9	570	0.050	71
29.6	1110	—	—
31.4	1210	0.047	74
38.9	1800	0.042	77

The latent heat of fusion per gram is found to be 25 cal.

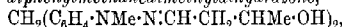
J. F. S.

**The Liquid Crystals of Agaricic Acid.** PAUL GAUBERT (*Compt. rend.*, 1919, **168**, 277—279).—Agaricic acid gives two types of liquid crystals, one belonging to the cubic system and the other being optically uniaxial and positive. The crystals are but slightly birefringent, and consequently the polychroism is feeble.

W. G.

**Phytochemical Reductions. XV. The Conversion of Acetaldo into Optically Active  $\beta$ -Butylene Glycol by Yeast.** CARL NEUBERG and (MME.) ELISABETH KERB (*Biochem. Zeitsch.*, 1918, **92**, 96—110).—The reaction,  $\text{OH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CHO} \rightarrow \text{OH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$ , takes place in the presence of yeast both when actively fermenting sugar and when, also, sugar is not added. A dextrorotatory product was obtained. The  $\beta$ -butylene glycol was, amongst other methods, characterised by preparing the di- $\alpha$ -naphthylurethane derivative, m. p.  $154^\circ$ , by its treatment with  $\alpha$ -naphthylcarbimide.

A method is given for preparing in good yield acetaldo by the action of disodium sulphite on aldehyde in the cold (at  $-15^\circ$ ). From the aldol were prepared the  $\beta$ -bromophenylhydrazone,  $\text{C}_{10}\text{H}_{13}\text{ON}_2\text{Br}$ , white, seemingly hexagonal leaflets, m. p.  $127$ — $128^\circ$ , and also the diphenylmethanedimethyldihydrazone,



colourless plates, m. p.  $117^\circ$ .

S. B. S.

**Phytochemical Reductions. XVI. The Conversion of Citral into Geraniol by Yeast.** CARL NEUBERG and (MME.) ELISABETH KERB (*Biochem. Zeitsch.*, 1918, **92**, 111—123).—This reaction takes place both in the presence and absence of added sugar. The geraniol which is produced is accompanied by some optically active substance which has not yet been identified. The authors describe the two following derivatives of cyclocitral: the thiosemicarbazone,  $\text{C}_{11}\text{H}_{19}\text{N}_3\text{S}$ , white leaflets, m. p.  $200$ — $201^\circ$ , and the *p*-nitrophenylhydrazone,  $\text{C}_{16}\text{H}_{21}\text{O}_2\text{N}_3$ , orange crystals, m. p.  $125^\circ$ .

S. B. S.

**Preparation of Soluble Starch.** A. LEULIER (*J. Pharm. Chim.*, 1918, [vii], 18, 291).—Twenty-five grams of starch are boiled for fifteen minutes under a reflux apparatus with a mixture of 100 grams of 95% alcohol and 5 grams of sulphuric acid; the starch is then collected on a filter and washed with water or alcohol until free from acidity. Starch thus treated is insoluble in cold water, but very soluble in hot water. [See, further, *J. Soc. Chem. Ind.*, 1919, 86A.]

W. P. S.

**The Preparation of Methylamine from Chloropicrin.** PERCY FARADAY FRANKLAND, FREDERICK CHALLENGER, and NOEL ALBERT NICHOLLS (*T.*, 1919, 115, 159—162).

**The Present Condition of the Benzene Problem.** HERMANS PAULY (*J. pr. Chem.*, 1918, [ii], 98, 106—135).—The various representations suggested for the benzene molecule are discussed. From a consideration of the relationships between the physical constants of benzene derivatives, the corresponding hydrogenated compounds, etc., the following conclusions are drawn: (1) The atoms of the benzene molecule lie in one plane. (2) The benzene ring must be symmetrically arranged and the linkings uniform. (3) Neither centric nor olefinic linkings are present, the degree of saturation of the linkings being approximately midway between those of simple and double linkings. Thiele's formula, the valence-electronic representation of benzene, the tetrahedral model, and the problem of orientation are also considered.

T. H. P.

**II-10-Bromophenanthrene-3- or -6-sulphonic Acid.** HÄRAN SANDQVIST (*Annalen*, 1918, 417, 1—16).—A hot aqueous solution of potassium phenanthrene-3-sulphonate is cooled to about 50° until crystals begin to separate, and a solution of bromine in water saturated at the ordinary temperature (about 3 mols. of bromine) is added gradually, whereby is obtained, in addition to oxidation products, potassium II-10-bromophenanthrene-3- or -6-sulphonate. The crude salt is converted through the chloride into II-10-bromophenanthrene-3- or -6-sulphonic acid,  $C_{14}H_9Br \cdot SO_3H \cdot 4H_2O$ , an almost white, non-crystalline mass, m. p. 152—153°, or, anhydrous, 223° (in a closed capillary, m. p. 160—170°), which has an astringent but, unlike the I-isomeride (*A.*, 1917, i, 552), no sweet taste, forms yellow, flocculent solutions, and shows some tendency to form liquid crystals. The potassium, ammonium, sodium, calcium, barium, and copper salts are described. The methyl ester, flattened needles, has m. p. 158°, the ethyl ester, needles, has m. p. usually 143.5°, but sometimes 134° (to a turbid liquid); the former yields methyl phenanthraquinone-3-sulphonate by oxidation with chromic and acetic acids. II-10-Bromophenanthrene-3- or -6-sulphonyl chloride, prepared from the potassium salt, forms faintly yellow prisms, m. p. 199—199.5°, from which are prepared the amide,  $C_{14}H_{10}O_2NBrS$ , needles, m. p. 266.5°, and the anilide, needles of leaflets, m. p. 211°.

C. S.

**I-10-Chlorophenanthrene-3- or -6-sulphonic Acid and 10-Chlorophenanthrene.** HÅKAN SANDQVIST (*Annalen*, 1918, 417, 17—33).—It has been shown (A., 1917, i, 552) that the abnormal viscosity and anisotropy of solutions of I-10-bromophenanthrene-3- or -6-sulphonic acid disappear when the bromine is replaced by the  $\cdot\text{SO}_3\text{H}$  or  $\cdot\text{C}_{14}\text{H}_7\text{Br}\cdot\text{SO}_3\text{Me}$  group. It is now found that they are increased when the bromine is replaced by a chlorine atom.

I-10-Chlorophenanthrene-3- or -6-sulphonic acid, prepared by fusing together I-10-bromophenanthrene-3- or -6-sulphonyl chloride and phosphorus pentachloride, and heating the resulting chloride with water at about  $145^\circ$ , forms a white, microcrystalline powder possessing an acid, sweet, astringent taste. A 0.04*N*-solution has a viscosity 1.03 at  $18^\circ$  (water at  $18^\circ=1$ ); this is increased to about 140 by the addition of one-sixth volume of 3*N*-hydrochloric acid, the value for I-10-bromophenanthrene-3- or -6-sulphonic acid being increased only to about 6 by similar treatment. The air-dried acid, m. p.  $160\text{--}161^\circ$ , contains  $3\text{H}_2\text{O}$  (decomp.); the anhydrous acid has m. p.  $206\text{--}207^\circ$ . The ammonium, sodium, potassium, calcium, barium, and copper salts are described. The methyl ester, leaflets or prisms, has m. p.  $172\text{--}172.5^\circ$ , and the ethyl ester, colourless crystals, m. p.  $182.5\text{--}183^\circ$ . The chloride,  $\text{C}_{14}\text{H}_9\text{Cl}\cdot\text{SO}_3\text{Cl}$ , prepared as above, forms prisms, m. p.  $196\text{--}197^\circ$ , and from it have been obtained the amide, needles, m. p.  $281\text{--}282^\circ$ , and anilide, crystals, m. p.  $197\text{--}198^\circ$ .

10-Chlorophenanthrene,  $\text{C}_{14}\text{H}_9\text{Cl}$ , m. p.  $35\text{--}55^\circ$  (purest specimen,  $52.5\text{--}53.5^\circ$ ), b. p.  $343\text{--}346^\circ$ , is obtained, together with other products (of which 9:10-dichloroanthracene and 9:10-phenanthrene dichloride have been identified), by adding a cold solution of chlorine (26 grams) in carbon disulphide to phenanthrene (50 grams) dissolved in the same solvent. It yields phenanthraquinone by oxidation, forms a picrate,  $\text{C}_{14}\text{H}_9\text{Cl}\cdot\text{C}_6\text{H}_5(\text{NO}_2)_3\cdot\text{OH}$ , yellowish-red needles, m. p.  $111\text{--}112^\circ$ , and is converted by sulphonation at  $165\text{--}170^\circ$  into a sulphonic acid, from which the preceding I-10-chlorophenanthrene-3- or -6-sulphonyl chloride, m. p.  $196\text{--}197^\circ$ , can be prepared. C. S.

**The Mobility of the Methylnitroamino-group in the Derivatives of Tetranitrophenylmethylnitroamine and in Trinitrodi(methylnitroamino)benzene.** C. F. VAN DUIN (*Rec. trav. chim.*, 1919, 38, 89—100).—A study of the action of ammonia, aniline, and *m*-nitroaniline on certain derivatives of 2:3:4:6-tetranitrophenylmethylnitroamine obtained by substituting the nitro-group in position 3 by an hydroxyl, an anilino-, a methylnitroamino-, an amino-, and a dimethylamino-group. The results show that a negative substituent in this position hinders the substitution of the methylnitroamino-group, whilst a positive substituent increases its mobility. As opposed to this, however, is the fact that in 2:4:6-trinitro-3-dimethylamino-phenyl-

methylnitroamine, the methylnitroamino-group is not replaced by *m*-nitroaniline.

In the action of ammonia on 2:4:6-trinitro-1:3-di(methylnitroamino)benzene, two compounds, one having m. p. 195—196° (corr.) and the other having m. p. 144° (corr.), were obtained, but could not be characterised. W. G.

**The Formation of Phenol in the Action of Sodium Methoxide on the Higher Chlorobenzenes.** P. W. DE LANGE (*Rec. trav. chim.*, 1919, **38**, 101—105. Compare Holleman and Mooy, A., 1916, i, 22).—The author finds that *p*-chloroanisole and *p*-dichlorobenzene when heated in sealed tubes at 176—177° with sodium methoxide in methyl alcohol each yielded *p*-chlorophenol and methyl ether, the reaction being far more complete with the *p*-chloroanisole than with the dichlorobenzene. He considers that the reaction with dichlorobenzene takes place in two stages, as follows:

- (1)  $C_6H_4Cl_2 + NaOMe = C_6H_4Cl \cdot OMe + NaCl$ .
- (2)  $C_6H_4Cl \cdot OMe + NaOMe = C_6H_4Cl \cdot ONa + Me_2O$ .

W. G.

**Velocity of Nitration of Phenols in Ethereal Solution. II.** ALFONS KLEMENC and ELISABETH EKL (*Monatsh.*, 1918, **39**, 641—696. Compare A., 1914, i, 272).—The velocity constants of the nitration of phenol, guaiacol, *o*- and *p*-cresol, and resorcinol methyl ether have been determined. Nitration is, in general, found to be a positive autocatalytic process, and the rate of nitration is dependent on the proportion of nitrogen peroxide or nitrous acid in the nitric acid. From this point of view, a mathematical expression for the velocity of nitration of a benzene derivative has been developed which, when applied to the particular case of phenols, takes into account the fact that the nitrous acid formed during the course of nitration (the cause of the autocatalytic nature of the process) is itself absorbed by the phenol.

Pure nitric acid, free from nitrogen peroxide and nitrous acid, does not cause nitration. Nitrogen peroxide induces both the nitrating and oxidising action of nitric acid towards derivatives of benzene.

In the case of nitration in ethereal solution, action either does not occur at all or rapidly comes to an end if the number of molecules of nitric acid is greater than that of the phenol or guaiacol, this behaviour being, apparently, opposed to the law of mass action.

The necessary solutions are obtained by dissolving anhydrous nitric acid in dry ether at a temperature of -80° (solutions prepared in this manner remain colourless at 0° for weeks), and by dissolving nitrogen peroxide in the same solvent in a special form of apparatus, which is figured in the text and allows the necessary adjustment of concentration and removal of known amounts of solution. The course of the reaction is followed by

determining the decrease in the titre of the nitric acid at given intervals. In the case of phenol, this can be done directly with standard barium hydroxide solution (the nitrophenol behaving as indicator) during the early stages of the reaction; during the later stages, the end-point is obscured by coloured bye-products, and it is then preferable to shake the ethereal solution with saturated potassium chloride solution and to add potassium hydroxide or barium hydroxide until the nitric acid is neutralised, when the next drop extracts a portion of the nitrophenol from the ether and colours the aqueous solution deep red. In the cases of guaiacol and other phenols, this method cannot be used, and recourse must be had to the iodometric process previously described (*loc. cit.*).

In addition to the phenols already mentioned, experiments with catechol, resorcinol, and quinol are also described. In the first two cases, satisfactory results could not be obtained; with quinol, the initial reaction consisted in the evolution of nitric oxide and formation of quinhedrone, which gradually underwent nitration. It is noteworthy that the presence of nitrogen peroxide is here found to be essential to the oxidising action of the nitric acid.

H. W.

**Oxidation of Quinol and its Sulphonic Acids by means of Fehling's Solution.** JOH. PINNOW (*J. pr. Chem.*, 1918, [ii], 98, 81—95. Compare A., 1911, i, 339).—Further experiments show that, when oxidised by Fehling's solution in absence of air, quinol and its sulphonic acids require almost exactly 3 atoms of oxygen per molecule, and give dihydroxyquinol or its sulphonic acids. The less amount of Fehling's solution earlier found sufficient with low concentrations of quinol (compare Bourquelot and Fichtenholz, A., 1910, i, 273) is explained by concurrent oxidation at the expense of atmospheric oxygen. In presence of sulphite, quinol and its sulphonic acids are oxidised by means of Fehling's solution principally to dihydroxyquinoldisulphonic acid, 5 or 4 atoms, respectively, of oxygen being used; this oxidation proceeds by way of quinone, quinolsulphonic acid, quinonesulphonic acid, and quinoldisulphonic acid, and not by way of dihydroxyquinone and its sulphonic acids. Unlike quinone and its sulphonic acids, dihydroxyquinone and its sulphonic acids do not unite with sulphite. Part of the quinol, which is not oxidised by Fehling's solution to the readily separable dihydroxyquinonedisulphonate, yields a readily soluble, pale-coloured isomeride, but the most important side reaction is the action of the alkali on the quinone-sulphonate, which should lead through hydroxyquinolsulphonate to the final product of oxidation, hydroxyquinonesulphonate.

T. H. P.

**Some Derivatives of Resorcinol.** H. VERMEULEN (*Rec. trav. chim.*, 1919, 38, 106—111).—2-Nitroresorcinol when added to nitric acid (D 1·5) in the cold yields 2:4-dinitroresorcinol, m. p. 146°, which when converted into its potassium salt and heated with an excess of methyl sulphate gives 2:4-dinitro-1:3-dimethoxy-

benzene; this, when reduced with tin and hydrochloric acid in alcoholic solution and the product treated with acetic anhydride, gives 2-nitro-4-acetyl-amino-1:3-dimethoxybenzene, m. p. 161–162°. This compound on nitration yields 2:6-dinitro-4-acetyl-amino-1:3-dimethoxybenzene, m. p. 129°, which when hydrolysed gives 2:6-dinitro-4-amino-1:3-dimethoxybenzene, m. p. 141°. 4-Acetyl-amino-1:3-dimethoxybenzene, m. p. 117°, when nitrated in acetic acid solution yields 6-nitro-4-acetyl-amino-1:3-dimethoxybenzene, m. p. 173°, which is also obtained by the acetylation of 6-nitro-4-amino-1:3-dimethoxybenzene, m. p. 136–137°, obtained by the reduction of 4:6-dinitro-1:3-dimethoxybenzene. W. G.

**Acetylsalicylic [*o*-Acetoxybenzoic] Acid.** HENRY L. DAWN (*J. Ind. Eng. Chem.*, 1919, 11, 29–30).—The melting point of aspirin is determined by immersion of the capillary tube in a stirred paraffin oil bath heated at the rate of 1° per minute, the thermometer being immersed during the whole time of heating but the melting-point tube inserted only when the temperature reaches 130°. The free salicylic acid present may be determined by comparison of the colour given with dilute ferric chloride with a series of cobalt chloride solutions of various concentrations. [See *J. Soc. Chem. Ind.*, 1919.] T. H. P.

**The Elimination of the Carbethoxyl Group from Tautomeric Systems. I. Derivatives of Indene.** CHRISTOPHER KELK INGOLD and JOCELYN FIELD THORPE (*T.*, 1919, 115, 143–159).

**Preparation of Mercury Derivatives of Phthaleins and Analogous Compounds.** SACCHARINFABRIK AKT.-GES. VORM. FAHLBERG, LIST, & Co. (D.R.-P. 308335; from *Chem. Zentr.*, 1918, ii, 881–882).—Neutral solutions of the alkali salts of phthaleins, succineins, and "sacchareins" are boiled with a large excess of a mercuric salt, particularly mercuric chloride, whereby uniform products are formed in an easily isolable condition. Thus, fluorescein and mercuric chloride yield a reddish-brown product, insoluble or sparingly soluble in the usual organic media, soluble in sodium carbonate, sodium hydroxide, or ammonia, to deep red solutions, which show a strong, greenish-yellow fluorescence when diluted. The ammoniacal solution is blackened by ammonium sulphide at its boiling point. The sodium salt of methylfluorescein gives a pale brown derivative with mercuric chloride which dyes silk orange-yellow. Mercuriated compounds from dibromofluorescein, tetrabromofluorescein, tetraiodofluorescein, phenolphthalein, tetraiodophenolphthalein, quinolphthalein, hydroxyquinolphthalein, resorcin succinein, cresorcin succinein, and resorcin saccharein are also described. H. W.

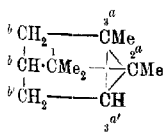
**The Reduction of Aromatic Ketones.** W. D. COHEN (*Rev. trav. chim.*, 1919, 38, 72–88).—In acid solution, benzophenone is reduced with the formation of benzopinacol, benzhydrol not being formed. If the action is energetic, a little diphenylmethane is

formed. In an alkaline medium, on the other hand, benzhydrol is almost exclusively obtained unless the alkali is very weak, in which case a little benzopinacone is formed. An energetic reduction produces some diphenylmethane. In neutral medium, as when reduced by aluminium amalgam in alcohol, benzophenone yields 68% of benzhydrol and 32% of benzopinacone. W. G.

**Preparation of  $\beta$ -Anthrimides.** FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.P. 308666; from *Chem. Zentr.*, 1918, ii, 882).—The products of the action of ammonia on  $\beta$ -diazanthraquinones are heated in solvents of high boiling point with or without a condensing agent. Thus, anthraquinone- $\beta$ -diazonium sulphate is made into a paste with alcohol and treated with well-cooled, concentrated alcoholic ammonia; the product is heated with nitrobenzene under reflux, when  $\beta\beta'$ -dianthrime separates as a dark brownish-red substance, which becomes yellowish-brown when dried or acidified; it forms a scarlet solution in concentrated sulphuric acid, which gradually becomes olive and then green. The product from 1:3-dibromoanthraquinone- $\beta$ -diazonium sulphate and alcoholic ammonia gives *tetrabromo- $\beta$ -dianthrime* (partly as the benzoyl derivative, which is hydrolysed with concentrated sulphuric acid) when heated to gentle boiling with nitrobenzene and benzoyl chloride. The substance is yellow and yields a bluish-green solution in concentrated sulphuric acid; it dyes cotton yellow from a reddish-brown bath. *Dichlorobisdiazanthraquinoneamide* (from diazotised 1-chloro-2-aminoanthraquinone and ammonia in excess) is pale yellow, and is converted by treatment with boiling nitrobenzene and benzoyl chloride into 1:1'-*dichloro-2:2'-dianthrime*, orange-yellow, matted needles soluble in concentrated sulphuric acid to a pure blue solution; it dyes cotton orange-yellow from a reddish-brown bath. H. W.

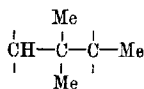
***sec.*- $\beta$ -Methylcamphor and *sec.*- $\beta$ -Phenylcamphor, a New Series of Synthetic Camphors, and *tert.*-Naphthylborneol and Naphthylcamphene.** J. BREDT (*J. pr. Chem.*, 1918, [ii], 98, 96–105).—In consequence of the publication of Ruzicka's paper (A., 1918, i, 398), the author gives a short account of work carried out in 1914–1918.

[With MARIA SAVELSBERG.]—The action of magnesium methyl iodide on camphor or on fenchone yields the tertiary alcohols, naphthylborneol and methylfenchol, which; under the action of lehydrating agents, yield one and the same hydrocarbon,  $C_{11}H_{18}$ , b. p. 172–175°, m. p. 71–73°, which shows great stability towards permanganate, and is regarded as a homocyclene of the annexed structure. When treated with acetic and sulphuric acids, the hydrocarbon yields an *acetyl* compound,  $C_{13}H_{20}O_2$ , b. p. 106–107°/13 mm., and this on hydrolysis gives a secondary alcohol,  $C_{11}H_{20}O$ , m. p. 193°, which forms a *phenylurethane*, m. p. 102°; oxidation of the alcohol yields a





ketone ( $\beta$ -methylcamphor),  $C_{11}H_{18}O$ , m. p. 167—168°, giving an oxime, m. p. 125—127°, and a semicarbazone, m. p. 255° (decomp.), and yielding 2-methylcamphoric acid,  $C_{11}H_{18}O_4$ , m. p. 191°, the anhydride of the acid has m. p. 205.5—207°. The properties of these products indicate that they belong to the camphor series, so that, in the splitting of the trimethylene ring of the hydrocarbon (see formula above), the linking  $3^a-3^a'$  is ruptured. This indication is confirmed by the molecular refraction of the ethyl ester of the acid; this ester has  $D_4^{20}$  1.0289, which differs but little from the value,  $D_4^{20}$  1.0298, for ethyl camphorate, whereas ethyl isofenchocamphorate has  $D_4^{20}$  1.0054. The specific exaltation of the molecular refraction of the ester of the new acid,  $E\Sigma_D = -0.229$ , is similar to that,  $-0.18$ , for ethyl camphorate, and is conditioned by the annexed grouping, whilst in ethyl isofenchocamphorate the grouping  $\text{CH}-\text{CH}_2-\text{C}-\text{Me}$  pre-

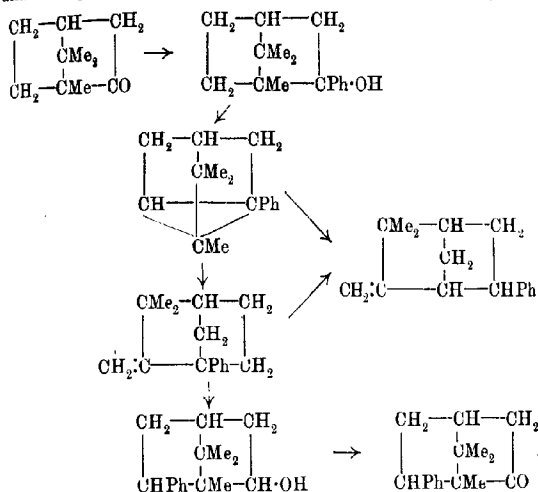


duces no exaltation. The following further derivatives of the 2-methylcamphoric acid were prepared: the dichloride, b. p. 155°/15 mm., the chlorinated chloride, the chloro-anhydride, m. p. 204—206°, the sec.-tert.-amino-acid, m. p. 162—163°, and its calcium salt, and the acid imide, m. p. 256°.

[With A. C. HEINEMANN and F. GOBLET.]—The interaction of magnesium phenyl bromide and camphor, followed by treatment of the product with water and dilute hydrochloric acid, yields the tert.-phenylborneol, m. p. 41°, b. p. 119.5—120.5°/2—2.5 mm.,  $[\alpha]_D^{20} = -50.33^\circ$  (in benzene), already prepared by Haller. Treatment of this tertiary alcohol with acetic anhydride gives a liquid hydrocarbon,  $C_{16}H_{20}$ , b. p. 99°/2 mm.,  $D_4^{20}$  0.9920,  $[\alpha]_D^{20} + 3.27^\circ$ , which is converted into the acetyl derivative of a tertiary alcohol, b. p. 136°/2 mm., m. p. 87°. This hydrocarbon partly undergoes rearrangement to an isomeride, b. p. 86°/2 mm.,  $D_4^{20}$  1.0034,  $[\alpha]_D^{20} - 3.75^\circ$ , whilst a third isomeride, b. p. 106°/2 mm., m. p. 33—34.5°,  $D_4^{20}$  0.9742, is formed in good yield on repeated dry distillation of the above acetyl compound. The hydrocarbon, b. p. 99°/2 mm., does not combine with hydrogen chloride in light petroleum solution, but the isomeride, b. p. 86°, forms the hydrochloride,  $C_{16}H_{21}Cl$ , m. p. 76.5°, which with milk of lime gives a tertiary alcohol,  $C_{16}H_{20}O$ , b. p. 106.5°,  $[\alpha]_D^{20} + 23.06^\circ$ , isomeric with the tert.-phenylborneol. Hydrolysis of the above acetyl derivative yields a secondary alcohol,  $C_{16}H_{20}O$ , m. p. 115—116°, which, like the products derived from it, is optically inactive. Oxidation of this alcohol by means of chromic acid gives a phenylcamphor,  $C_{16}H_{20}O$ , m. p. 68°, the formation of which takes place as shown on p. i, 127.

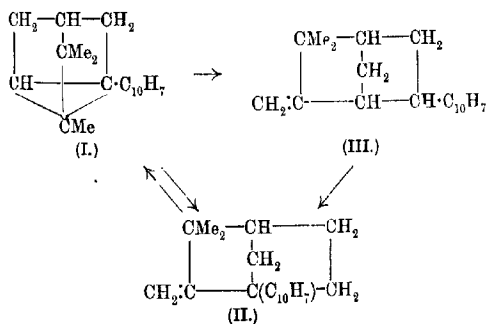
The new phenylcamphor forms a semicarbazone, m. p. 189—190°, and an oxime, m. p. 141—142.5°, and when reduced with sodium and alcohol gives a mixture of phenylborneol and phenylisoborneol, which were not separated. With sodiopotassamide and amyl nitrite, phenylcamphor yields the isonitroso-derivative, which forms

reenish-white crystals, m. p. 189°, and this with sodium hydrogen sulphite gives *phenylcamphorquinone*, a golden-yellow substance, m. p. 145°. The latter is also obtained by the action of permanganate on *phenylcamphorcarboxylic acid*, m. p. 149–150° (evolu-



tion of  $\text{CO}_2$ ), which is formed from phenylcamphor with the help of sodiopotassamide and carbon dioxide. *Phenylcamphoric acid*,  $\text{C}_{16}\text{H}_{20}\text{O}_4$ , m. p. 123.5°, is formed by the protracted action of permanganate solution on the quinone; its *anhydride*,  $\text{C}_{16}\text{H}_{18}\text{O}$ , m. p. 173.5°, was prepared.

[With H. DUSSIER.]—The action of magnesium  $\alpha$ -naphthyl bromide on camphor yields *tert.-naphthylborneol*, m. p. 122–124°,

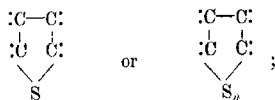


$[\alpha]_D^{25} -41.96^\circ$  in benzene. When subjected to dry distillation, this alcohol yields the *naphthylcamphene*,  $C_{20}H_{32}$ , which crystallises in felted needles, m. p.  $92-93^\circ$ , b. p.  $210^\circ/16$  mm., and gives no hydrochloride with dry hydrogen chloride in ethereal solution. Treatment of the hydrocarbon with acetic and sulphuric acids yields only an *isomeride*, m. p.  $116-117^\circ$ . From results obtained with methylocycloene and phenylcamphene, it may be assumed that the *naphthylcamphene*, m. p.  $92-93^\circ$ , has structure I or II, and that treatment with acetic and sulphuric acids, under the influence of the *naphthyl* residue, leads to rearrangement to the compound III, which cannot be acetylated.

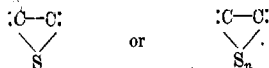
T. H. P.

### Condensation of Unsaturated Compounds in Relation to Terpenes, Resins, and Caoutchouc.

H. J. PRINS (*Chem. Weekblad*, 1919, 16, 64-74).—The type of condensation discussed is that between molecules of the same substance containing the group  $:C=C:$ . The reaction is brought about by catalysts, such as acids, acid anhydrides, halogens and halogen compounds with active halogen, sulphur and sulphur compounds (persulphides), oxygen and peroxides, metallic oxides, and metals. The catalyst and substrate are "reciprocally activated." Three reactions are possible: polymerisation of the unsaturated substance, combination of catalyst with the substance at the double bond, and combination of catalyst with the polymerised substance formed. The theory of reciprocal activation is discussed in relation to the simultaneous polymerisation and oxidation of unsaturated hydrocarbons, such as terpenes, the formation of resins, and the vulcanisation of caoutchouc. The following theory for the last-mentioned process is suggested. The caoutchouc molecule is rendered active by means of the catalyst sulphur, whilst the sulphur undergoes a change analogous to the formation of ozone from oxygen in presence of unsaturated substances. There results (1) a simple polymerisation of the caoutchouc molecule with formation of *cyclobutane* derivatives; (2) polymerisation of the caoutchouc molecule with inclusion of sulphur in the ring, giving compounds of the type



(3) direct addition of sulphur at the double bond to form :



W. S. M.

**Constituents of Resins. III. Further Investigation of Siarresinol from Siamese Gum Benzoin.** ALOIS ZINKE and HANS LIEB (*Monatsh.*, 1918, 39, 627-639).—It has been previously shown that the benzoresinol obtained by Lüdy from

Sumatra gum benzoin (A., 1893, i, 480—666) is probably a mixture of *d*-sumaresinol and *l*-benzoiresinol (A., 1918, i, 502); further examination of the substance prepared according to Lüdy's directions only led to the isolation of siaresinol (A., 1918, i, 398). Lüdy's benzoiresinol should therefore be deleted from the literature.

Further examination of *d*-sumaresinol and siaresinol has shown that these substances are acidic in character, and that the acidic hydrogen is contained in the carboxyl, and not in the hydroxyl group as assumed by Lüdy (*loc. cit.*); the former is therefore to be regarded as *d*-sumaresinolic acid and the latter as *d*-siaresinolic acid. Oxidation of *d*-siaresinolic acid leads to the formation of a monobasic acid,  $C_{27}H_{40}O_4$ , and the loss of three atoms of carbon and eight atoms of hydrogen appears to denote the elimination of a propyl or an isopropyl group; the formula for the parent substance may be written  $C_9H_7 \cdot C_{26}H_{40}O_2 \cdot CO_2H$ .

[With LUDWIG ZECHNER.]—Silver siaresinolate forms a white powder which darkens in colour when preserved, and decomposes when warmed with water, acetone, or alcohol. It is converted by methyl iodide into methyl siaresinolate, which crystallises in prismatic crystals with  $1\frac{1}{2}H_2O$  from aqueous alcohol, m. p. about  $150^\circ$ , in needles with  $\frac{1}{2}H_2O$  from benzene, and in anhydrous, prismatic crystals, m. p.  $169$ — $170^\circ$ , from light petroleum. The ethyl ester separates from light petroleum in needles or prismatic platelets, m. p.  $108^\circ$ ; from aqueous alcohol in nodular masses, which melt indefinitely at  $102^\circ$  and contain water of crystallisation. The mixed anhydride of acetic and siaresinolic acids melts at  $125$ — $127^\circ$  after softening at  $104^\circ$ .

Chromic acid oxidises the double compound of acetic and *d*-siaresinolic acid to an acid,  $C_{27}H_{40}O_4$ , short prisms, m. p.  $317^\circ$ ,  $[a]_D^{20} = -193.8^\circ$  in chloroform solution; the potassium salt, long, white needles with  $3\frac{1}{2}H_2O$ , and the methyl ester, colourless leaflets, m. p.  $186$ — $187^\circ$ , are described. H. W.

**Hydroxymethylfurfuraldehyde.** J. A. MIDDENDORP (*Rec. trav. chim.*, 1919, **38**, 1—71).—The author finds that *o*-hydroxymethylfurfuraldehyde, obtained by the action of acids on the hexoses, can be distilled unchanged in an absolute vacuum, giving a distillate, b. p.  $114$ — $116^\circ/1$  mm., which will crystallise and has m. p.  $31.5^\circ$ ,  $D_4^{20} 1.268$ ,  $D_4^{25} 1.2629$ ,  $n_D^{20} 1.556$ ,  $n_D^{25} 1.552$ ,  $n_D^{30} 1.563$ , and its heat of combustion is  $664.8$  cal. per gram-mol. Contrary to the general statements, the author finds that this aldehyde is miscible with water in all proportions, and that there is no indication of the formation of a hydrate. It gives a phenylmethylhydrazone, m. p.  $161^\circ$ , and an aldzine, m. p.  $168^\circ$  (decomp.), and its hydroxyl group may readily be replaced by halogen by the action of the hydrogen halide in dry ether. *o*-Chloromethylfurfuraldehyde is readily converted into *o*-methoxymethylfurfuraldehyde, an oil, b. p.  $68$ — $70^\circ/2$  mm.,  $D_4^{17.5} 1.146$ ,  $n_D^{20} 1.5088$  giving a phenylhydrazone, m. p.  $56$ — $57^\circ$ , a *p*-nitrophenylhydr-

azone, m. p. 140—141°, an oxime, an aldazine, m. p. 86°, a *semicarbazone*, m. p. 170°, and a *semioxamazone*, m. p. 209—210°. Similarly, *o*-ethoxymethylfurfuraldehyde gives a *p*-nitrophenylhydrazone, m. p. 140—141°, an oxime, an aldazine, m. p. 70°, and a *semioxamazone*, m. p. 212—213°. Benzoyloxymethylfurfuraldehyde gives a phenylhydrazone, m. p. 112°, a *p*-nitrophenylhydrazone, m. p. 142°, an oxime, m. p. 85—85.5°, an aldazine, m. p. 163°, a *semicarbazone*, m. p. 198°, and a *semioxamazone*, m. p. 204° (decomp.).

When distilled at a pressure of 10—20 mm., hydroxymethylfurfuraldehyde is partly decomposed, giving its anhydride, difurfurylmethyl ether, which yields a *semicarbazone*, m. p. 255°, and when oxidised by moist silver oxide gives di(2-methyl-5-carboxylfuryl) ether, m. p. 165°.

Sodium hydroxide readily decomposes hydroxymethylfurfuraldehyde, giving 2:5-dihydroxymethylfuran, m. p. 80°, and 5-hydroxymethylpyromucic acid. Under similar conditions, methoxymethylfurfuraldehyde gives 2-hydroxymethyl-5-methoxymethylfuran, b. p. 132—134°/23 mm., m. p. 37°,  $n_D^{20}$  1.4860, and 5-methoxymethylpyromucic acid, m. p. 66—66.5°; the ethoxy-aldehyde similarly gives 2-hydroxymethyl-5-ethoxymethylfuran, b. p. 152—157°/20 mm.,  $n_D^{20}$  1.4865, and 5-ethoxymethylpyromucic acid, m. p. 62°.

Hydroxymethylfurfuraldehyde condenses with ethyl malonate, giving ethyl hydroxymethylfurfurylidene malonate, m. p. 48.5°, b. p. 221°/11 mm.,  $D_D^{20}$  1.1648,  $n_D^{20}$  1.539,  $n_D^{25}$  1.536, and with malonic acid, giving hydroxymethylfurfurylidene malonic acid, decomposing at 130°.

Ammonia or potassium cyanide react readily in alcoholic solution with hydroxy-, methoxy-, or ethoxy-methylfurfuraldehyde, but the products in every case resinify.

From a study of the absorption spectra of the coloured products obtained from furfuraldehyde and its methyl and hydroxymethyl derivatives, respectively, with the following reagents, resorcinol, Sesamé oil,  $\beta$ -naphthol, acetone, diphenylamine, egg-albumin, aniline acetate, narcotine, and orcinol, it is shown that the coloured products formed by warming sucrose with hydrochloric acid and the respective reagents resemble those obtained from hydroxymethylfurfuraldehyde, but differ from those obtained from furfuraldehyde itself. It is shown that diphenylamine is the most satisfactory reagent for distinguishing between pentoses and hexoses, and that the reaction with acetone is the most satisfactory for distinguishing methylpentoses from pentoses and hexoses. W. G.

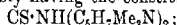
**The Alkaloids of *Holarrhena congolensis*.** FRANK LE PYMAN (T., 1919, 115, 163—166).

**Nicotine Content of the Smoke of Heavy, Light, and "Nicotine-free" Cigars.** W. STORM VAN LEEUWEN (*Arch. exp. Path. Pharm.*, 1918, 84, 282—316).—This content was measured

physiologically by the effect on the blood-pressure of an acid extract of the smoke, and bears no relationship to the trade description or even to the nicotine content of the cigars themselves. The smoke of so-called nicotine-free cigars (Wendt) contains as much as that of average normal ones. A full account of earlier work is given.

G. B.

**Cyclic Acetone Bases.** C. HARRIES (*Annalen*, 1918, 417, 107—191. Compare A., 1896, i, 317).—The author has shown that vinylacetoneamineoxime (4-oximino-2:2:6-trimethylpiperidine) yields  $\alpha$ -4-amino-2:2:6-trimethylpiperidine by reduction with zinc dust and cold alcoholic hydrochloric acid, and  $\beta$ -4-amino-2:2:6-trimethylpiperidine by reduction with sodium and boiling amyl alcohol (*loc. cit.*, and A., 1897, i, 293). These two bases behave differently towards carbon disulphide. Whilst the  $\beta$ -base yields only one dithiocarbamate which cannot be converted into a thiocarbimide by mercuric chloride, the  $\alpha$ -base yields an easily soluble dithiocarbamate, which is changed by boiling water into a sparingly soluble dithiocarbamate; from the last, hot aqueous mercuric chloride solution produces a substance which has the composition of the expected thiocarbimide, but not its properties, and is therefore probably an internal thiocarbimide. By treatment with iodine, the two  $\alpha$ -dithiocarbamates (2 mols.) lose carbon disulphide (1 mol.) and hydrogen sulphide (1 mol.) and yield two isomeric thiocarbamides, probably having the constitution



these are probably syn- and anti-stereoisomerides, and so also are the two  $\alpha$ -dithiocarbamates.

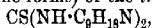
The question why the  $\beta$ -base does not yield an analogous series of isomerides cannot be answered at present.

[With A. BAUDREXEL, H. HOHENEMSER, and R. HAARMANN.]—Between 1896 and 1908, the reduction of 4-oximino-2:2:6-trimethylpiperidine to  $\alpha$ -4-amino-2:2:6-trimethylpiperidine by cold alcoholic hydrogen chloride and zinc dust has frequently been effected. It is all the more remarkable, therefore, that the authors, using present-day zinc dust (since 1913), have obtained, not the above  $\alpha$ -base, but 2:2:6-trimethyl-4-piperidone. In order to prepare the  $\alpha$ -base, therefore, 4-oximino-2:2:6-trimethylpiperidine has been reduced by 3% sodium amalgam in 80% alcoholic solution at 10—20°, 25% hydrochloric acid being constantly added to maintain an acid reaction. This method produces about equal weights of  $\alpha$ - and  $\beta$ -4-amino-2:2:6-trimethylpiperidine; the hydrochloride of the latter is insoluble in absolute alcohol.

[With BERNHARD SCHELLHORN.]—Whether reduced by cold alcoholic hydrochloric acid and zinc dust or by boiling amyl alcohol and sodium, 4-oximino-2:2:6-tetramethylpiperidine yields only one 4-amino-2:2:6:6-tetramethylpiperidine, leaflets, m. p. 16—18°, b. p. 79°/7 mm., which is converted by acetic anhydride into the acetate of the acetylamino-derivative, m. p. 205°; the acetylamino-

derivative itself,  $C_{11}H_{20}ON_2$ , forms pyramidal crystals, m. p.  $120^\circ$ , b. p.  $161-163^\circ/6-8$  mm.

In cold ethereal solution, 4-amino-2:2:6:6-tetramethylpiperidine (2 mols.) and carbon disulphide (1 mol.) yield 4-amino-2:2:6:6-tetramethylpiperidine 2:2:6:6-tetramethylpiperidylthiocarbamate,  $C_9H_{18}N \cdot NH \cdot CS \cdot SH$ ,  $C_9H_{18}N \cdot NH_2$ , crystals, m. p.  $154^\circ$ , but in the ratio of 1:1 yield tetramethylpiperidylthiocarbamic acid,  $C_9H_{18}N \cdot NH \cdot CS \cdot SH$ , m. p.  $180^\circ$ ; this, and also the preceding salt, are converted into a substance, m. p.  $205^\circ$  (decomp.), by recrystallisation from boiling water. The dithiocarbamic acid in boiling aqueous-alcoholic solution is converted by alcoholic iodine into the hydriodide (two crystalline forms) of the thiocarbamide,



triangular plates, m. p.  $170^\circ$ .

Corresponding with the production of two alkamines by the reduction of 2:2:6-trimethyl-4-piperidone (Harries, A., 1897, i, 293), it is found that 2:2-dimethyl-6-isobutyl-4-piperidone, reduced by sodium amalgam in faintly acid solution, yields a mixture of labile *cis-valerdiacetonalalkamine* [4-hydroxy-2:2-dimethyl-6-isobutylpiperidine],  $NH < \begin{array}{c} CH(CH_3Pr^3) \cdot CH_2 \\ | \\ CMe_2 \end{array} > CH \cdot OH$ , m. p.  $91-92^\circ$  (hydrochloride, m. p.  $215^\circ$ ), and the stable *trans-isomeride*, m. p.  $65^\circ$ ; the former is converted into the latter by heating with a solution of sodium amyl oxide.

2:2-Dimethyl-6-isobutyl-4-piperidone forms an *oxime*,  $C_{11}H_{20}ON_2$ , needles, m. p.  $121^\circ$  (*monohydrochloride*, m. p.  $238^\circ$ ; *dihydrochloride*, needles, m. p.  $222^\circ$ ), which is reduced by sodium and boiling amyl alcohol to 4-amino-2:2-dimethyl-6-isobutylpiperidine,  $C_{11}H_{24}N_2$ , b. p.  $147^\circ/65$  mm. (*hydrochloride*,  $C_{11}H_{24}N_2 \cdot 2HCl$ ; *acetate* of the acetyl derivative, m. p.  $143-144^\circ$ ). The base yields a carbamate by absorption of carbon dioxide, and is converted by nitrous acid into the preceding *cis*-alkamine, m. p.  $91-92^\circ$ .

By warming with acetic anhydride, 2:2:6-trimethyl-4-piperidone is converted into its *acetyl* derivative, prisms, m. p.  $92^\circ$ , which yields *acetylvinylidiacetonamineoxime* (1-acetyl-4-oximino-2:2:6-trimethylpiperidine), m. p.  $130^\circ$ , by treatment with aqueous hydroxylamine.

[With A. ZART.]—Benzylidenediacetonalamineoxime yields only products of fissive decomposition when reduced by zinc dust and alcoholic hydrochloric acid, but is converted by reduction with sodium and boiling amyl alcohol into  $\beta$ -4-amino-2-phenyl-6:6-dimethylpiperidine, six-sided plates softening at  $60^\circ$ , no definite m. p., b. p.  $183^\circ/36$  mm., which is isolated as the *hydrobromide*,  $C_{18}H_{20}N_2 \cdot 2HBr$ , prisms with  $3H_2O$ , m. p.  $75^\circ$ , decomp.  $100^\circ$ ; the *hydrochloride*, *platinichloride*, *hydriodide*, and *picrate* are mentioned.

[With AUGUST BAUDREXEL.]— $\alpha$ -4-Amino-2:2:6-trimethylpiperidine and ethyl chloroformate react in cold ether to form the *hydrochloride*,  $C_{11}H_{22}O_2N_2 \cdot HCl$ , crystals, m. p.  $244-245^\circ$ , of

*α*-ethyl trimethylpiperidylcarbamate, b. p. 148—150°/12 mm. (picrate, m. p. 208—209°). Attempts to eliminate ethyl alcohol from the carbamate with the object of creating a bridge linking in the 1:4-position were unsuccessfully made with zinc chloride, fused sodium acetate, phosphoric anhydride, phosphoryl chloride, and concentrated hydrochloric acid. The *α*-aminotrimethylpiperidine reacts in ethereal solution with carbon dioxide to form the carbamate,  $C_5H_7Me_3N \cdot NH \cdot CO_2H \cdot NH_2 \cdot C_5H_7Me_3N$ , m. p. 112°.

The following compounds of the *β*-series were prepared by similar methods: *β*-ethyl 2:2:6-trimethylpiperidyl-4-carbamate, b. p. 151—152°/12 mm., m. p. 68°, and its hydrochloride, m. p. 253—254° (decomp.), and picrate, m. p. 164—165°; *β*-aminotrimethylpiperidine trimethylpiperidylcarbamate, m. p. 92°.

[With A. ZART.]—*α*- and *β*-4-Amino-2:2:6-trimethylpiperidine yield dibenzoyl derivatives,  $C_{22}H_{29}O_2N_2$ , m. p. 192—193° and 210—211° respectively, on benzoylation. The *α*-base reacts with phenylcarbimide in cold benzene to form the phenyltrimethylpiperidylcarbamide,  $NHPh \cdot CO \cdot NH \cdot C_5H_7Me_3N$ , needles, m. p. 211—212°, and with phenylthiocarbimide in ethereal solution to form the corresponding thiocarbamide,  $C_{15}H_{23}N_3S$ , crystals, m. p. 110°, whilst the hydrochloride of the *α*-base reacts with potassium cyanate in concentrated aqueous solution to form *α*-trimethylpiperidylcarbamide,  $C_5H_7Me_3N \cdot NH \cdot CO \cdot NH_2$ , leaflets, m. p. 55° (not sharp), decomp. below 100°. The corresponding substances in the *β*-series are phenyltrimethylpiperidylcarbamide, m. p. 130—138°, the thiocarbamide,  $C_{15}H_{23}N_3S$ , m. p. 160—161°, and *β*-trimethylpiperidylcarbamide, m. p. 170—171°.

[With HERBERT THOERL.]—Equal molecular quantities of 2:2:6-trimethyl-4-piperidone and ethyl chloroformate in ethereal solution, heated on the water-bath with a saturated solution of potassium carbonate, yield ethyl 4-keto-2:2:6-trimethylpiperidine-1-carboxylate, m. p. 34—35°, b. p. 141—142°/12 mm. (oxime, leaflets, m. p. 136°). The oxime is reduced by sodium amalgam and a mixture of alcohol, water, and acetic acid on the water-bath to ethyl 4-amino-2:2:6-trimethylpiperidine-1-carboxylate, b. p. 160°/12 mm., from which an internal 1:4-carbamide could not be produced.

The direct methylation of 2:2:6-trimethyl-4-piperidone at the imino-group is very difficultly effected. The result is attained indirectly, however, by oxidising *α*- and *β*-*N*-methylvinylidiacetonalkamines (see below) by chromic and acetic acids. Although the *α*-isomeride is very resistant to oxidation, both yield the same *N*-methylvinylidiacetonamine (1:2:2:6-tetramethyl-4-piperidone), b. p. 96—97°/14 mm., which is purified through the hydrobromide. It forms an oxime, prisms, m. p. 93° (picrate, needles, m. p. 216° [decomp.]).

[With AUGUST BAUDREXEL.]—The following derivatives have been prepared with the object of obtaining substances suitable for



the easy identification of the more important cyclic acetone bases, but none of them compares with the oxime for this purpose. 2:2:6-Trimethyl-4-piperidone forms a *semicarbazone*,  $C_9H_{15}ON_2$ , crystals, m. p. 196—197° (*oxalate*, m. p. 182°), the triacetoneamine forms a *semicarbazone*,  $C_{16}H_{20}ON_4$ , crystals, m. p. 219—220°, whilst benzylidenediacetoneamine forms a *p-nitrophenylhydrazone*,  

$$C_{16}H_{23}O_2N_4$$

m. p. 105—106°.

[With ARTHUR ZART.]—4-Hydroxy- $\alpha$ - and - $\beta$ -1:2:2:6-tetramethylpiperidines are readily obtained by heating the 4-hydroxy-2:2:6-trimethylpiperidines with 40% formaldehyde on the water-bath. The hydrochloride of the  $\alpha$ -compound reacts with benzoyl chloride at 120° to form  $\alpha$ -4-benzoyl-1:2:2:6-tetramethylpiperidine, b. p. 194—195°/16 mm. (*hydrochloride*, m. p. 192°, *platinichloride*, m. p. 208° [decomp.], *nitrate*, and *picrate*, m. p. 180—181°). The corresponding  $\beta$ -benzoyl derivative has b. p. 195°/15 mm., and forms a *hydrochloride*, m. p. 58° (not sharp), *platinichloride*, m. p. 218° (decomp.), *nitrate*, m. p. 163° (decomp.), and *picrate*, m. p. 213°.

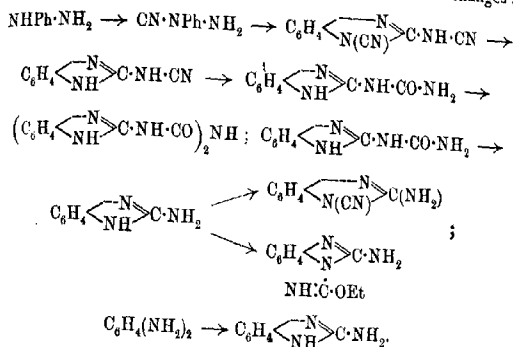
[With ERICH GROSCHUFF.]—The behaviour of cyclic acetone bases towards nitrous acid has been already published (A., 1901, i, 745). C. S.

**New Mode of Formation of Pyrrole-black.** A. ANGELI and A. PIERONI (*Atti R. Accad. Lincei*, 1918, [v], 27, ii, 300—304. Compare A., 1918, i, 547).—Treatment of pyrrole with the calculated quantity of magnesium ethyl iodide in very dilute ethereal solution, and passage through the liquid of a gentle current of air for about twenty-four hours, yields a voluminous, very black powder, which may be obtained almost free from ash by treatment with dilute sulphuric acid. This substance is far more intensely black than the pyrrole-blacks obtained by methods previously described, and, like these and the natural melanins, it does not melt, but furnishes vapours which turn a pine splinter moistened with hydrochloric acid an intense red; it is insoluble in all ordinary solvents, and also in alkali solutions. It is slowly oxidised by hydrogen peroxide in acetic acid, or dilute aqueous permanganate, or dichromate and dilute sulphuric acid. The compositions of the different pyrrole-blacks obtained in various ways are given. The yellowish-white product formed, together with pyrrole-black, by the action of peracetic acid, is probably a derivative of tripyrrole, and its composition is in agreement with the formula  $C_{12}H_{17}O_3N_3$ . Like aniline-blacks, pyrrole-blacks react readily with phenylhydrazine.

T. H. P.

**Action of Cyanogen Haloids on Phenylhydrazine. IV. Passage to Derivatives of  $\alpha$ -Phenylenediamine.** G. PELLIZZANI and AUGUSTO GAITER (*Gazzetta*, 1918, 48, ii, 151—182).—Further

investigations (compare A., 1892, 1323; 1907, i, 873 and 1911, i, 338) show that it is possible to effect the following series of changes:



*αβ-Dicyano-o-phenyleneguanidine*,  $\text{C}_6\text{H}_4\langle\text{N}\rangle_{\text{N(CN)}}\text{C}\cdot\text{NH}\cdot\text{CN}$ , obtained by the action of cyanogen bromide on *α*-cyanophenylhydrazine in presence of water and pieces of marble, forms white crystals, and turns yellow and then brown when heated, but does not melt at 300°; it reacts acid towards litmus, and emits ammonia when heated with alkali hydroxide. The sodium salt forms a crystalline magma, and the potassium salt a gelatinous mass.

*β-Cyano-o-phenyleneguanidine*,  $\text{C}_6\text{H}_4\langle\text{N}\rangle_{\text{NH}}\text{C}\cdot\text{NH}\cdot\text{CN}$ , prepared by the action of potassium hydroxide on the preceding compound, forms long, thin, elastic, shining needles, and turns yellow at 240° and softens and decomposes at 250–260°; it has slightly acid properties and exhibits normal ebullioscopic behaviour in alcohol. It is highly resistant to the action of potassium hydroxide, and only in a sealed tube at 140° is it possible to detach the *β*-cyanogen group. Its *silver* salt was prepared and analysed.

*o-Phenylene-β-guanylcarbamide*,  $\text{C}_6\text{H}_4\langle\text{N}\rangle_{\text{NH}}\text{C}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , obtained as hydrochloride by the action of hot dilute or cold concentrated hydrochloric acid, forms shining, colourless needles and becomes opaque, but does not melt at 300°. Its *hydrochloride*,  $\text{C}_6\text{H}_4\text{ONH}_2\cdot\text{HCl}$ , decomposing at 255–260°, *platinichloride*, and *picrate* were prepared and analysed.

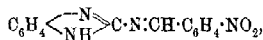
*Diphenyleneguanylbiuret*,  $(\text{C}_6\text{H}_4\langle\text{N}\rangle_{\text{NH}}\text{C}\cdot\text{NH}\cdot\text{CO})_2\text{NH}$ , obtained by heating the preceding compound at 180–200°, crystallises in slender needles.

*o-Phenyleneguanidine*, prepared by the action of hydrochloric acid on *o*-phenyleneguanylcarbamide or *αβ*-dicyano-*o*-phenylene-

guanidine, is identical with the compound obtained from cyanogen bromide and *o*-phenylenediamine (compare Pierron, A., 1906, i, 926). The following salts were prepared and analysed: *carbonate*; *nitrate*, exploding without melting at 225°; *acetate*, m. p. 218°; *picrate*, m. p. 270° (decomp.); and *platinichloride*, + 3H<sub>2</sub>O, which softens at 225°, and then melts and decomposes. The free base may be recognised by the alkaline reaction of its aqueous solution towards litmus and by the intense blue coloration, changing to green and then to brownish-yellow, obtained by the action of hypobromites or hypochlorites.

*Acetyl-o-phenyleneguanidine*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \text{NH} \end{smallmatrix} \text{C} \cdot \text{NHAc}$ , forms slender, white needles, m. p. 314–315° (decomp.). The action of nitrous acid on the corresponding benzoyl derivative (compare Pierron, *loc. cit.*) yields phenylenecarbamide,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \text{NH} \end{smallmatrix} \text{C} \cdot \text{OH}$  or  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix} \text{CO}$ .

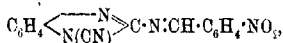
*m-Nitrobenzylidenephenyleneguanidine*,



prepared from *o*-phenyleneguanidine and *m*-nitrobenzaldehyde in presence of a drop of piperidine, forms minute, yellow needles, m. p. 170°.

*α-Cyano-o-phenyleneguanidine*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \text{N(CN)} \end{smallmatrix} \text{C} \cdot \text{NH}_2$ , obtained from *o*-phenyleneguanidine and cyanogen bromide, forms long, colourless needles, and decomposes at 173–175°, rapidly in a moist atmosphere and slowly in a desiccator. Its *platinichloride* turns brown at 100° and undergoes change when boiled with water.

*m-Nitrobenzylidene-α-cyano-o-phenyleneguanidine*,



prepared by the interaction of *α*-cyano-*o*-phenyleneguanidine and *m*-nitrobenzaldehyde in alcoholic solution in presence of a drop of piperidine, forms microscopic, yellow crystals and decomposes at 285–290°.

*α-Ethoxy-o-phenylenecarbaminoguanidine*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \text{C} \cdot \text{NH}_2$



obtained together with the preceding compound, forms colourless needles, m. p. 155°. Its *platinichloride* forms pale yellow rhombs, m. p. 222–224° (decomp.). With *m*-nitrobenzaldehyde in presence of a drop of piperidine, the base yields *m-nitrobenzylidene-α-ethoxy-o-phenylenecarbaminoguanidine*, C<sub>17</sub>H<sub>15</sub>O<sub>3</sub>N<sub>5</sub>, which crystallises in pale yellow needles, m. p. 205–206° (decomp.).

According to Pierron (*loc. cit.*), the action of cyanogen bromide (3 mols.) and sodium hydrogen carbonate (3 mols.) on *o*-phenylene-

diamine (1 mol.) yields a little phenyleneguanidine and a large proportion (120—140% of the phenylenediamine used) of iminodi-

carbonylphenyleneguanidine,  $\text{C}_6\text{H}_4$  This

compound may be obtained also from phenyleneguanidine (1 mol.), cyanogen bromide (2 mols.), and sodium hydrogen carbonate (2 mols.), or from phenyleneguanidine and biuret. The mechanism of its formation is under investigation.

T. H. P.

**Simultaneous Biochemical Syntheses of Gentiobiose and of the two  $\beta$ -Glucosides of Glycol by Emulsin.** Em. BOURQUELOT and M. BRIDEL (*Compt. rend.*, 1919, 168, 253—256).

—From the products of the action of emulsin from almonds on a mixture of dextrose and ethylene glycol, in the molecular proportion of 2:1, in aqueous solution, the authors have isolated and characterised gentiobiose, glycol  $\beta$ -glucoside, and glycol  $\beta$ -diglucoside.

W. G.

## Physiological Chemistry.

**The Blood Sugar.** GUSTAV KROK (*Biochem. Zeitsch.*, 1918, 92, 84—89).—An analysis of the sugar in blood was made by Bang's micro-method, both before and after hydrolysis by acids in the case of rabbits, after ingestion of starch and of maltose (at varying intervals), and after administration of adrenaline, and a few similar analyses were made on the blood of the human subject. There was no appreciable difference in the reducing power before and after hydrolysis in any case, and the results give no support to Lépine's conception of the "sucre virtuel" of blood.

S. B. S.

**The Theory of Clotting.** ALFRED PERUTZ and MAX ROSEMAN (*Biochem. Zeitsch.*, 1918, 92, 90—95).—The amount of fibrin which is obtained by mixing serum and plasma stands in some proportional relationship to the amounts of these two components used, when they are employed in great dilutions. If diminishing amounts of serum are added to the same amount of plasma, the amount of fibrin formed diminishes. In the same way, diminishing amounts of plasma added to the same amount of serum also produce diminishing amounts of fibrin. If very great dilutions are employed of plasma and serum, so as to be near the limits of a reaction, in order that the reaction should take place at all, the serum concentration must be greater than the plasma concentration.

S. B. S.

**The Presence of Phosphates in Human Blood-serum.** VII. JOH. FEIGL (*Biochem. Zeitsch.*, 1918, **92**, 1—83).—The author gives a very extensive and detailed review of the methods of separating the constituents which contain phosphorus in the blood, especially the lipid phosphorus and inorganic (acid soluble) phosphorus, giving in particular a detailed criticism of the recent methods of Bloor, Greenwald, and their collaborators. He also gives a critical account of the micro-methods for estimating the phosphorus after ashing, including the various nephelometric and colorimetric methods. He gives, finally, a series of tables of analyses of the phosphorus of the blood (chiefly lecithin phosphorus) in pathological cases obtained by himself by the employment of various methods.

S. B. S.

**Shark and Ray Liver Oils.** M. TSUJIMOTO (*J. Chem. Ind. Tokyo*, 1918, **21**, 1015—1042).—The analytical values of the liver oils of thirteen species of Japanese sharks and five species of Japanese rays are given. The oil derived from the shark *Pristiurus pilosus* had an exceptionally high iodine value (309.0) and a very low sp. gr. ( $D_4^{20}$  0.8664). It was found that all the shark liver oils of low sp. gr. (below 0.9) contained the hydrocarbon squalene, which was also present in the egg oils of two species of shark, but it was not a constituent of any of the ray liver oils. [See also *J. Soc. Chem. Ind.*, 1919, 109A.]

C. A. M.

**Genesis of Thiocyanic Acid in Animals.** V. SERAFINO DEZANI (*Arch. Farm. sper. sci. aff.*, 1918, **25**, 278—288; from *Chem. Zentr.*, 1918, ii, 836—837).—The quantity of thiocyanic acid formed in the dog depends on the albumin content of the food; this result is in striking contrast with the experience of Bruylants and Grober with the human subject.

After administration of acetonitrile, thiocyanic acid could be detected in the blood serum and saliva of the dog as soon as in the urine; its formation cannot therefore in any case be an exclusive function of the kidneys.

H. W.

**Calcium—Form of Reserve in the Female of the Phasmides; its Forms of Elimination in the two Sexes.** J. PANTEL (*Compt. rend.*, 1919, **168**, 242—244).—Calcium exists as a reserve in the form of its carbonate in the lower malpighian tubes of the females of the Phasmides. In both sexes, the principal form in which it is eliminated is as its phosphate, accessory forms being the oxalate and probably the urate.

W. G.

**Catalytic Action of Serpent Venoms on the Nucleic Acids.** C. DELEZENNE and H. MOREL (*Compt. rend.*, 1919, **168**, 244—246).—Both plant and animal nucleic acids are hydrolysed by venoms from members of the Colubridae and Viperidae groups. The curves showing the velocity of the reaction indicate that the reaction is catalytic, and it has been shown that the amount of

hydrolysis is independent of the amount of venom used. The optimum temperature is 50—52°, and the venom loses its hydrolytic powers if heated for a few minutes at 100° or if to the medium is added specific antivenom serum. The different venoms vary in the intensity of their catalytic action, this variation being in the same direction as is that of their toxicity.

W. G.

**The Guttameter and its Application to the Study of Drugs and Poisons.** FRIEDRICH ESCHBAUM (*Ber. Deut. pharm. Ges.*, 1918, 18, 397—416).—The guttameter is a capillary pipette with a wide delivery orifice from which ten drops are collected in a weighing bottle and the weight recorded. The instrument is standardised with water at 20°, ten drops of which should weigh 1.20 grams. The weight of ten drops of the liquid, corrected by the factor of standardisation of the instrument, is proportional to the surface tension; thus the results are inversely proportional to those obtained with the stalagmometer. The author has extended certain observations of Traube and others on the use of this instrument, from which it was deduced that the toxicity of solutions of alkaloids is in direct relation to the lowering of the surface tension of water produced by the alkaloid at standard concentration. Thus a number of derivatives of the quinine alkaloids have been studied and ranged in the order of decrease in surface tension produced in 0.1% solutions of their salts mixed with increasing small proportions of sodium carbonate. The order of classification so obtained coincides with that of increasing toxicity. Quinine and quinidine, approximately equal, had the least effect on surface tension; stronger depressions were recorded in the following order: hydroquinine, ethylhydrocupreine, ethylapohydroquinidine, isomethylhydrocupreine, and isocetylhydrocupreine. The depression of the surface tension increases with the amount of alkali added. Morphine and apomorphine occupy a peculiar position among the alkaloids in that solutions of their salts, when treated with sodium carbonate, do not show a depression of the surface tension as compared with water. It is shown, however, that morphine salts when treated with certain small proportions of ammonia liberate the alkaloid in a disperse form, and a depression of the surface tension is then observed.

J. F. B.

## Chemistry of Vegetable Physiology and Agriculture.

**Action of Stimulants on Nitrifying Bacteria.** C. MONTANARI (*Staz. sper. agr. ital.*, 1917, 50, 69—72; from *Chem. Zentr.*, 1918, ii, 854. Compare A., 1914, i, 1159).—The action of compounds of copper, barium, lead, zinc, and arsenic has been investigated in extension of the work on manganese salts. The addition produces

different effects according as it takes place at the commencement of the experiment or when development of the nitrate ferment has occurred. In the former case, the formation of nitrates is hindered by small amounts of copper or by larger quantities of the other substances, whilst in the latter case the ferment is damaged by large doses of arsenic or, to some extent, of copper. Nitrification was not rendered more vigorous by minimal doses of the different substances, except in the solitary instance of manganese sulphate.

H. W.

**The Chemistry of the Higher Fungi. XIII. *Scleroderma vulgare*, Fr., and *Polysaccum crassipes*, D.C.** JULIUS ZELLNER (*Monatsh.*, 1918, **39**, 603—615. Compare A., 1915, i, 1086; 1918, i, 54).—Extraction of *Scleroderma vulgare*, Fr., with light petroleum yielded a deep brown, viscous mass containing an ergosterol and a resin. The ethereal extract contained fumaric acid, and further quantities of an ergosterol, which was not isolated in the pure state. Mannitol, dextrose, choline, and an amorphous carbohydrate were isolated from the alcoholic extract. Viscosin and potassium phosphate were isolated from the aqueous extract, in which neither invertases nor diastases could be detected.

*Polysaccum crassipes*, D.C., was similarly successively extracted with (1) light petroleum, (2) ether, (3) alcohol, and (4) water. The first extract was a dark brown, viscous mass rich in unsaponifiable matter, consisting of ergosterols and a reddish-brown resin. The second extract consisted of ergosterols; the presence of fumaric acid could not be definitely established. The third extract yielded dextrose, choline, and the potassium ammonium salt of a tannin-like acid (the free acid and its silver and copper salts are described), which probably has a glucosidic structure. The fourth extract contained a carbohydrate similar to that obtained from *Scleroderma*, together with mineral matter; the presence of ferments (invertase, maltase, diastase) could not be established.

H. W.

**The Researches of Willstätter on the Assimilation of Carbon Dioxide.** H. I. WATERMAN (*Chem. Weekblad*, 1918, **15**, 1138—1146).—A critical summary of the more recent work of Willstätter on the mechanism of the absorption and decomposition of carbon dioxide by chlorophyll.

W. S. M.

**Action of Vegetable Enzymes on certain Organic Compounds.** G. CIAMICIAN and C. RAVENNA (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 293—300).—Much of this paper has been already published, the results not included in the previous abstract (this vol., i, 58) being briefly as follows.

Benzoic acid is not changed by the enzymes of pulped spinach leaves, but salicylic acid is largely oxidised; the respective sodium salts behave similarly. Coumarin remains unaltered, but mandelic acid is converted by spinach in an atmosphere of oxygen into a

compound which is not extracted by ether, but is reconverted into the original acid by boiling dilute sulphuric acid; in carbon dioxide, mandelic acid remains unaffected. Just as by the action of light, oxalic acid is almost completely oxidised by the enzymes, whilst succinic acid, which in the light is oxidised to a slight extent to glyoxal, acetaldehyde, acetic, and perhaps propionic acid, with the spinach enzymes yields acetaldehyde and a compound giving succinic acid when treated with emulsin. Lactic acid, which forms acetaldehyde and acetic acid on auto-oxidation in the light, yields only acetaldehyde under the action of the spinach. Malic acid, which gives formaldehyde, acetaldehyde, formic and acetic acids, and certain undefined products under the influence of light, yields only acetaldehyde with these enzymes.

Acetone is oxidised, as by light, to acetic and formic acids and formaldehyde, whilst methyl ethyl ketone gives propionic and formic acids under the influence of the spinach, its behaviour in light being unknown. The action of light on cyclic ketones results in hydrolysis to the corresponding aliphatic acids, and also in the formation of the corresponding dibasic or ketonic acids, whereas the action of the spinach enzymes converts these ketones into lower aliphatic acids and sometimes into succinic acid, the acids corresponding with the ketones used being never obtained. Thus, *cyclohexanone* gives formic acid and a mixture of volatile acids, apparently propionic and butyric. 2-Methyl*cyclohexanone* and 3-methyl*cyclohexanone* yield propionic and formic acids, and 4-methyl*cyclohexanone*, acetic acid, in addition. Menthone gives succinic, formic, acetic, and probably propionic acids. Pyridine, piperidine, nicotine, strychnine, and caffeine are not affected by the spinach enzymes, but morphine, quinine, and cinchonine undergo oxidation to a considerable extent.

Some of the compounds, such as benzoic acid, pyridine, piperidine, and nicotine, which resist attack by the enzymes of spinach, disappear when they are injected into maize and tobacco plants (*loc. cit.*). In one experiment, in which a total of 36 grams of sodium benzoate, corresponding with 30.5 grams of benzoic acid, were inoculated into twenty-five maize plants, 21.6 grams of the acid were afterwards found to have disappeared, and the plants yielded a distillate containing formic, acetic, and propionic acids in amounts corresponding approximately with the benzoic acid attacked.

T. H. P.

**Biochemical Changes due to Environment.** ORRO ROSENHEIM (*Biochem. J.*, 1918, 12, 283—289).—The inflorescence of edelweiss (*Leontopodium alpinum*) contains a chromogenic substance, probably a flavone, which is not in glucosidic combination. It is best extracted with 90% alcohol at 70—75°. A comparative estimation of the amount present in plants grown in London at an altitude of 80 m. and in plants collected in the Alps at an altitude of 2000 m. shows the ratio of amounts present to be roughly as



1:4, and in addition the plants grown in the Alps contained traces of the chromogenic substance in glucosidic combination. These results show the biochemical adaptation of Alpine plants to changed environment, and support Shibata's hypothesis that the biological significance of flavones in the plant consists in their protective action against the injurious influence of ultra-violet light.

W. G.

**Essential Oil and Wax of Shuei Flower (*Jasminum odoratissimum*).** R. TSUCHIHASHI and S. TASAKI (*J. Chem. Ind., Tokyo*, 1918, 21, 1117—1143).—Fresh flowers of Shuei (*Jasminum odoratissimum*), cultivated in Formosa and used for perfuming tea, yielded on extraction with light petroleum 0.277% of concrete essence, which on maceration with alcohol was separated into 0.116% of essential oil and 0.166% of flower wax. The oil contained approximately 6% of *d*-linalool, 6% *d*-linalool acetate, 6% benzyl alcohol, 1.6% benzyl acetate, methyl ester of anthranilic acid and indole (10%), and constituents of high boiling point (possibly sesquiterpene alcohol or diterpene alcohol) about 57%. [See also *J. Soc. Chem. Ind.*, 1919, 117A.] C. A. M.

**The Absorbent Power of Dry or Moist Earth with respect to Chlorine Gas.** DANIEL BERTHELOT and RENÉ TRANNOY (*Compt. rend.*, 1919, 168, 121—123).—Dry sand absorbs chlorine badly, but a peaty soil or leaf mould has very marked absorbent properties for this gas. The absorptive power is markedly increased by moistening the soil with 10% of its weight of water. Any further addition of water only causes an increased absorption, due to the water added.

W. G.

**Connection between Absorption and Coagulation and its Relation to the Inorganic Colloids of the Soil. III.** A. DE DOMINICIS and P. CHIARIERI (*Staz. sper. agr. ital.*, 1917, 50, 451—479; from *Chem. Zentr.*, 1918, ii, 854. Compare A., 1915, i, 859; 1916, i, 240).—The previous results, that the action of electrolytes on the unstable hydrosols causes a single process resulting in coagulation through absorption, are confirmed by a series of experiments with the metals of the alkaline earths. When particles and ions with opposite charges come into contact, mutual attraction occurs, resulting in neutralisation of the charges and formation of absorption compounds. Decrease in concentration consequently follows both in colloidal and ionic-molecular solution. The physico-chemical properties of the soil are invariably favourably influenced with regard to fruitfulness by this phenomenon.

H. W.

**The Organic Phosphorus of Soil.** R. S. POTTER and R. S. SNYDER (*Soil Sci.*, 1918, 6, 321—332. Compare Potter and Benton, A., 1917, i, 76).—For the most part a reply to Gortner and Shaw (compare A., 1917, i, 376). The authors have prepared the curves for the hydrolysis of phytin and of nucleic acid by 5%

sulphuric acid at 100°, and show that both these reactions are of the first order. No definite conclusions could be drawn from the curves for the hydrolysis of the organic phosphorus of three soils, but the direction of the curves was such as to indicate that the organic phosphorus might have been due to phytin or to a pyrimidine nucleotide.  
W. G.

**The Presence of Aluminium as a Reason for the Difference in the Effect of so-called Acid Soil on Barley and Rye.** BURT L. HARTWELL and F. R. PEMBER (*Soil Sci.*, 1918, 6, 259—279).—The authors find that although rye will grow far more satisfactorily on an acid soil than will barley, seedlings of both these crops are equally affected by a given amount of acidity, both in water and sand cultures. The authors attribute the different effect of the acid soil on the two crops to the presence of aluminium sulphate in the soil solution, and they show that equivalent amounts of aluminium sulphate and sulphuric acid when added to an optimum nutrient solution produce about the same depression on barley seedlings, and that whilst a similar depression of the rye crop is produced by the acid, the aluminium sulphate causes very little depression and scarcely affects the rye roots. Further, as the hydrogen-ion concentration of the nutrient solution containing the aluminium sulphate was only about one-fourth of that containing the acid, they conclude that aluminium exerts a toxic effect on the barley. This active aluminium may be largely removed from the soil solution by the application of lime or phosphates, even acid phosphates.  
W. G.

**Experiments with various Nitrogenous Fertilisers.** EILH. ALFRED MITSCHERLICH, S. VON SAUCKEN, and F. IFFLAND (*J. Landw.*, 1918, 66, 187—198).—Sand cultures of oats were treated with one and the same fertiliser, composed of magnesium and potassium sulphates, sodium chloride, and calcium phosphate, the nitrogen in the different cultures of a series being supplied in the form of sodium nitrate, ammonium sulphate, "Kalkstickstoff," carbamide, and carbamide nitrate. The results show that carbamide and its nitrate are at least equivalent in manurial value to the old nitrogenous fertilisers. Owing to its ready solubility in water, carbamide nitrate should serve, without causing marked plasmolytic phenomena, and hence injuries to the plants, as an excellent top-dressing, and may certainly replace sodium nitrate for this purpose. The yields of straw and corn under the different treatments are given in the form of tables, and are also subjected to analysis.  
T. H. P.

**Influence of Two Different Nutriment on the Yield of Crops.** EILH. ALFRED MITSCHERLICH (*Landw. Jahrb.*, 1918, 52, 279—296; from *Chem. Zentr.*, 1918, ii, 854—856).—I. *Influence of two nutriment which are without mutual action.*—The effect of variation in the amounts of potassium and nitrogen on the growth

of oats has been investigated, use being made of potassium sulphate and ammonium nitrate. The factor of activity of the nitrogen is constant ( $=1.14$ ) and independent of the amount of potassium; similarly, the factor of the potassium ( $=2.48$ ) is constant and independent of the quantity of nitrogen. If the nutriment is present in an equally assimilable form (which may be assumed to be the case with salts which are soluble in water), and if they are not influenced by any external factor, it follows that, in order to secure an equal yield of oats, 2.18 times ( $2.48/1.14$ ) as much nitrogen as potash must be supplied; potassium is better utilised than nitrogen by the plant.

II. *Influence of two nutriment which react with one another.*

—Alterations in the increase in yield obtained by addition of either nutriment are immediately observed when the nutriment is either chemically or physically affected by other substances which are possibly introduced in the manuring, but which can be present in every possible combination in the soil in agricultural practice.

(a) *Chalk and phosphoric acid.*—Experiment shows that an equally good yield cannot be obtained by manuring with raw phosphate as with a readily soluble manure. Further, the maximum yield which can be obtained with a phosphate manure is diminished slightly at first, but more rapidly subsequently, by addition of chalk, and, finally, as is shown by experiments with phosphorite meal, to such an extent that an increase in yield due to the phosphate manure is scarcely noticeable. The value of different phosphate manures is affected in an extraordinary manner by the addition of chalk. Thus, the activity of tricalcium phosphate is diminished to considerably greater extent than that of a Thomas meal phosphate by addition of chalk; the value of the latter, however, does not remain constant, since a good specimen is found to be less affected than one of poorer quality. The relative value of tricalcium phosphate and Thomas meal T. in the absence of chalk is approximately the same as that previously found when calcium was added in large quantity in the form of calcium nitrate. Phosphatic manure loses much of its value if applied to land recently treated with chalk or marl or to soil rich in chalk unless other salts, such as ammonium sulphate, are also used. Manures which contain phosphates in a slightly soluble form are less effective in the presence of potash than those containing more soluble forms; raw phosphate is probably useless on land rich in chalk. It is doubtful if a preliminary manuring with phosphoric acid has any practical result. (b) *Potash and ammonium chloride.*—It has been previously found that the application of ammonium chloride, when sufficient nitrogen for nutriment is otherwise present, diminishes the value of manuring with potash; this result is now confirmed, and it appears to be not impossible that, under the given conditions, the ammonium chloride is physiologically acid, and therefore poisonous.

H. W.

## General and Physical Chemistry.

**Quantitative Spectra of Lithium, Rubidium, Cæsium, and Gold.** A. G. G. LEONARD and P. WHELAN (*Sci. Proc. Roy. Dubl. Soc.*, 1918, 15, 274—278).—The spark spectra of dilute solutions of the chlorides of lithium, rubidium, cæsium, and gold have been photographed with the object of ascertaining the persistency and intensity of the lines with dilution. The measurements were made with a single prism quartz spectrograph (Hilger). In the case of lithium chloride, the most persistent lines are  $\lambda\lambda$  6708.2 and 4602.5; these lines persist to a dilution 0.001%, whilst the line  $\lambda$  6103.8 only persists to 0.01%. The lines of rubidium chloride do not exhibit any remarkable persistency, only one,  $\lambda$  4571.8, appearing with a 0.1% solution. Solutions of cæsium chloride exhibit a fair number of lines, the most persistent being  $\lambda\lambda$  4593.5, 4555.5, 4540.2, and 2525.8, these all being visible in a 0.001% solution. The solution lines of gold chloride are not very persistent; no lines are visible in a 0.01% solution; the lines obtained from a 0.1% solution are  $\lambda\lambda$  4792.8, 4310.7, 3927.8, 3133.2, 3122.9, 2918.5, 2676.1, 2641.6, and 2201.4.

J. F. S.

**Gamma Ray Activity of Thorium-D.** HERBERT N. MCCOY and G. H. CARTLEDGE (*J. Amer. Chem. Soc.*, 1919, 41, 50—53. See this vol., ii, 120).—Two methods are described for the determination of the  $\gamma$ -ray activity of thorium-D. The first consists in measuring the activity of the sulphide in terms of a standard (0.355 mg. radium) and making emanation determinations by the method previously described (*loc. cit.*). The second method consists in sealing radiothorium precipitate in a crystallising dish and comparing with radium in a similar dish. As a mean value of the experiments, it is shown that  $\text{Th-D}:\text{Th}=0.956 \times 10^{-7}$ . Using the value found by McCoy and Henderson (A., 1918, ii, 422), that 1 gram of radium is equivalent to  $8.85 \times 10^6$  grams of thorium, it is shown that  $1.46 \times 10^{-7}$  grams of radium has the same  $\gamma$ -activity as 1 gram of thorium. Combining the  $\text{Ms}:\text{Th}$  ratio  $0.52 \times 10^{-7}$  with the present  $\text{Th-D}:\text{Th}$  ratio, the value  $1.48 \times 10^{-7}$  is the radium equivalent of the  $\gamma$ -products of thorium determined separately. Thorium-D therefore furnishes 1.81 times as much  $\gamma$ -activity as the mesothorium in equilibrium with the same amount of thorium. Taking account of the fact that only 35% of the thorium disintegrates into thorium-D, this means that, atom for atom, thorium-D contributes 5.17 times as much  $\gamma$ -activity as mesothorium.

J. F. S.

**Absorption of X-Rays.** TYCHO E:SON AURÉN (*Phil. Mag.*, 1919, [vi], 37, 165—207).—Making use of the method previously described (A., 1917, ii, 350), the author has determined the relative

absorption coefficients of a number of elements, including aluminium, iron, nickel, copper, and tin, and of a very large number of inorganic and organic compounds. In the case of the compounds, the additive law has been found valid throughout. With the possible exception of carbon, the state of aggregation appears to have no influence on the amount of adsorption. In examining chemical compounds in which the same element appears, but with differing valencies, it is shown that there is no difference in the quantity of absorption in any case. The relation between the atomic absorption coefficients for most elements has been determined at the medium wave-lengths  $\lambda = 0.38, 0.36, 0.34$ , and  $0.30 \times 10^{-8}$  cm. Assuming that absorption for hydrogen is exclusively due to scattering produced by the electron combined with the atomic nucleus, it has been found likely that scattering for other elements is solely due to the electrons constituting the outer layer of the respective atoms, that is, to the "outer electrons," and by aid of the relative atomic absorption coefficient for hydrogen, the number of the outer electrons has been estimated for the lighter elements. The atomic absorption coefficient increases for different elements by groups nearly proportionally to the atomic number. If it is accepted that the atomic number gives the number of electrons combined with the atomic nucleus, it is possible from the increase of absorption with increasing atomic number to determine the distribution of electrons between the outer and inner regions. From Barkla and White's determinations of the ratio  $\mu/\rho$  for copper and water, a formula of the mass scattering coefficient for different elements has been deduced. The values calculated for the relative absorption coefficients for  $\gamma$ -rays agree fairly with the observed absorption coefficients. The value of the mass scattering coefficient of aluminium for  $\gamma$ -radiation, calculated by means of the above-mentioned formula, agrees very nearly with the value directly observed by Ishino. The number of the outer electrons in the lighter elements seems to be the same for the elements placed in the same group of the periodic system, and the distribution of electrons thus appears to be in close connexion with the periodicity of the chemical qualities of the elements as expressed by this system.

J. F. S.

**Investigation of Röntgen Spectra. *M*-Series.** W. STENSTRÖM (*Ann. Physik*, 1918, [iv], 57, 347—375).—The author has investigated the *M*-series of Röntgen spectra for the elements uranium, thorium, bismuth, lead, thallium, gold, platinum, iridium, osmium, tungsten, tantalum, lutecium, ytterbium, erbium, holmium, and dysprosium. It is shown that the older method of measuring Röntgen spectra is not suitable for the soft radiations of the *M*-series, but that better results are obtained if a glowing cathode and high-frequency transformed alternating current are used. As cathode, a Wehnelt cathode was at first employed, but this was later replaced by a tungsten spiral. To find a grating of suitable constant, many crystals were examined and the constant

determined. These included rock salt,  $d=2.814 \times 10^{-8}$  cm.; potassium chloride,  $d=3.136 \times 10^{-8}$  cm.; calcite,  $3.028 \times 10^{-8}$  cm.; gypsum,  $7.621 \times 10^{-8}$  cm.; potassium ferrocyanide,  $8.454 \times 10^{-8}$  cm.; mica,  $10.1 \times 10^{-8}$  cm.; quartz,  $4.23 \times 10^{-8}$  cm.; beryl,  $4.61 \times 10^{-8}$  cm. (on plane 0.0.0.1) and  $8.06 \times 10^{-8}$  cm. (on plane 1.0.1.0); sodium ammonium tartrate,  $7.30 \times 10^{-8}$  cm.; sucrose,  $10.56 \times 10^{-8}$  cm.; and the compound,  $\text{AgNaC}_6\text{H}_5\text{O}_4\text{S}_2, \text{Na}_2\text{C}_6\text{H}_5\text{O}_4\text{S}_2, 10\text{H}_2\text{O}$ ,  $d=19 \times 10^{-8}$  cm. From a discussion of the sources of error, it is shown that the probable error of the measurements does not exceed 0.2–0.3%. The present measurements were made with a gypsum crystal, and it is shown that, in addition to the  $\alpha$ - and  $\beta$ -lines, a  $\gamma$ -line also exists in the  $M$ -series, and this conforms to the Moseley relationship. Other lines appear in some cases but these are in all probability due to impurities. Each of the main lines is diffuse and wide, and the blackening decreases with decreasing wave-length. They consist of several single lines, which were not sufficiently separated for characterisation.

J. F. S.

**Conductivity. IV. Conductivity of Alkaline Earth Formates in Anhydrous Formic Acid.** H. I. SCHLESINGER and R. D. MULLINIX (*J. Amer. Chem. Soc.*, 1919, **41**, 72–75. Compare A., 1912, ii, 26; 1914, ii, 703; 1916, ii, 210).—The electrical conductivity of solutions of calcium formate and strontium formate has been determined in anhydrous formic acid solutions at 25°. The conductivity concentration curves are composed of three parts—of two straight lines which intersect at about  $N/10$ , and a portion which curves upward in a manner similar to that observed for sodium formate (*loc. cit.*). It is likely that these salts ionise into a metal formate ion, which in more dilute solutions is decomposed into a simple metal ion, and that this second ionisation becomes sufficiently great at the concentrations where the two curves meet to affect the conductivity appreciably.

J. F. S.

**Depolarisers of the Becquerel Effect.** ALEXANDER VON SAMSONOW (*Zeitsch. wiss. Photochem.*, 1918, **18**, 141–176).—Working with oxidised copper electrodes, the author has studied the action of certain depolarisers on the electrode when immersed in solutions of sodium sulphate, bromate, iodate, and chlorate. The potential rises much higher in iodate and bromate solutions than in sulphate and chlorate solutions. As depolarisers, ferrous sulphate, glycine developer, sodium sulphite, iron oxalate, *p*-aminophenol, sodium arsenite, and sodium phosphite were used. Working hypotheses of the Becquerel effect and the action of the depolarisers are discussed.

J. F. S.

**Phenomenon of Electrical Supertension.** A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 375–381. Compare this vol., ii, 8).—A theoretical paper in which an unattainable electrode is considered as a hydrogen electrode from the point of

view of the phase rule. The supertension of electrodes is considered from the same point of view, and a  $\Delta$ - $x$  diagram is drawn to illustrate the process. It is shown that there is no essential difference between the phenomena of supertension and polarisation. The former is only a little more complicated in so far that here an unattackable electrode has been inserted into the system. When, however, the phenomenon of supertension is considered at attackable electrodes, the process becomes identical with that of polarisation.

J. F. S.

**Periodic Passivity of Iron. II.** A. SMITS and C. A. LOBRY DE BRAUYN (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 382—385. Compare A., 1917, ii, 262).—A continuation of previous work in which it was shown that anodically polarised iron could be activated by the introduction of halogen ions. Hence, by the electrolysis of a solution of ferrous sulphate and ferrous chloride, the phenomenon of passivity can be made periodic. This periodic property has now been photographically recorded, together with the time duration of each stage of the process. The potential difference varies between  $-0.3$  volt and  $+1.4$  volts with respect to the normal calomel electrode, and the current density changed from 33 milliamperes to 28 milliamperes per sq. cm. With a sealed-in electrode 1.5 cm. long, the iron was active for a short period and passive for a comparatively long period. With a smaller current density, the active and passive periods become nearly equal. The effects on the curves produced by changing the relative depth of the electrodes have been studied. Using a larger iron electrode, the potential difference showed irregular oscillations, whilst the current strength was regularly periodic. The irregularity was such that even the most active state did not recur regularly, and the whole curve shows periodicity under the influence of great disturbances. Hence it follows that the electrode was never active throughout the whole area at the same time. This confirms the previous view that the difficulty of rendering iron passive increases with increasing size.

J. F. S.

**The Sign of the Electrical Phenomenon and the Influence of Lyotropic Series observed in this Phenomenon.**

H. ZWAARDEMAKER and H. ZEEHUISEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 417—427. Compare A., 1918, ii, 351).—The nebula produced when an unsaturated solution of salicylic acid is sprayed always possesses a negative electric charge. This charge is weakened by both anions and cations, in the order  $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+ < \text{NH}_4^+$  for cations, and  $\text{CNS}^-, \text{NO}_3^-, \text{I}^-, \text{Cl}^-, \text{Br}^-, \text{C}_2\text{H}_3\text{O}_2^- < \text{tartrate ion} < \text{PO}_4^{3-} < \text{citrate ion} < \text{SO}_4^{2-}$  for anions. Acetic acid weakens or completely destroys the negative charge of salicylic acid. In higher concentrations with a positive electrical phase, it prevails as an acid over salicylic acid sprayed in weak solutions, which gives a negative charge. Acetates also have a weakening effect on the charge of salicylic acid, whereas of them-

selves they produce no charge. Mixtures of salicylic and acetic acids showed the electrical property of acetic acid so long as the latter acid is present in the larger quantity. If the concentration of acetic acid in the mixture falls so low that such a solution of acetic acid alone would give scarcely any effect, then the charge of the mixture sinks to zero; in still lower concentrations of acetic acid, the charge reappears, but this time negative. J. F. S.

**Dependence of the Magnetic Properties, the Specific Resistance, and the Density of Iron Alloys on their Thermal Treatment.** E. GÜMLICH (*Zeutsch. Elektrochem.*, 1918, **24**, 372—377).—The density, specific resistance, temperature coefficient of the resistance, the first and second transition points, and the magnetic properties (coercive force, retentiveness, permeability, and hysteresis loss) have been determined before and after annealing processes carried out under various conditions on pure electrolytic iron, commercial iron (seven specimens), iron alloys with carbon (0—1·8%), with silicon (0—8·5%), with aluminium (0—10·5%), and manganese (0—16%). In the case of pure iron, the following values were obtained:  $D$  7·876; specific resistance per sq. mm., 0·0994; temperature coefficient of the resistance between 20° and 100°, 0·01%; saturation value,  $4\pi I_s = 21,620$ , where  $I$  is the intensity of magnetisation. These values were very little changed by annealing and stand in contrast to the magnetic properties. It is shown that the improvement in the magnetic properties brought about by annealing is not due, as generally believed, to a molecular change, but rather to the removal of adsorbed gases. In rich carbon alloys, the first and second transition points lie in the same position as those given in the diagram of condition. In the curves between the carbon content and the density, coercivity and saturation value, respectively, there is a sharp break at the point where, normally, cementite separates from perlite or martensite. The carbon content has a marked effect on the coercive force. This quantity increases approximately 7 gauss per 1% increase in the carbon content in the case of perlite and 70 gauss in the case of martensite. With smaller carbon content, the influence is much greater; thus with 0·1% carbon impurity, the coercive force rises 0·7 gauss. The presence of silicon diminishes the magnetic properties; this substance behaves like non-magnetic impurities, which diminish the magnetic properties of the iron. The presence of aluminium affects the iron in much the same way as silicon; the specific resistance increases nearly proportionally to the aluminium content. The second transition point is lowered 100° by 10% of aluminium. The manganese alloys show similarities to the carbon alloys. The coercive force is extraordinarily high after annealing, and with 10% manganese has a value of 60 gauss, whereas the retentiveness disappears with 14—16% manganese. With manganese concentrations 8—9%, the density, specific resistance, and the magnetic properties show great irregularity. The transition points show a marked tempera-



ture hysteresis, and from this it is deduced that alloys containing 10—12% manganese cannot be magnetised. J. F. S.

**Diamagnetism in Weak [Magnetic] Fields.** O. E. FRIVOLD (*Ann. Physik*, 1918, [iv], 57, 471—488).—The magnetic susceptibility of tellurium, water, sulphur, antimony, zinc, gold, and silver has been investigated in magnetic fields of varying strength. With the exception of zinc, all the elements investigated show a dependence, with respect to their susceptibility, on the strength of the field for weak fields. In the case of higher field strengths, the susceptibility is constant except in the case of silver. The susceptibility is constant for field strengths down to 100 gauss in the case of zinc, to 600 gauss for gold, to 250 gauss for antimony, to 200 gauss for tellurium, and above 600 gauss for sulphur. Silver is paramagnetic in weak fields, but becomes diamagnetic in fields above 800 gauss. In the case of antimony, tellurium, and sulphur, a very strong dependence on the field strength for weak fields is displayed. The susceptibility of gold shows a dependence on the field strength which is in keeping with the theory of Gauss, and on the basis of this theory, the number of magnetons per cu. cm. has been calculated and the value  $1.7 \times 10^{14}$  obtained. Consequently, a magneton of gold contains  $3.65 \times 10^9$  atoms. J. F. S.

**The So-called First Quantum Theory of Planck. The Quantum Theory of Paramagnetism.** ADOLF SMEKAL (*Ann. Physik*, 1918, [iv], 57, 376—400).—A theoretical paper in which three formulæ are deduced to represent susceptibility. These formulæ are tested on measurements for ferric sulphate, manganese sulphate, and the tetrahydrate of manganese sulphate, and a comparison is made with the quanten theories of Planck. J. F. S.

**Thermal Conductivity of Neon.** S. WEBER (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, 21, 342—356).—The thermal conductivity of neon has been determined under various pressures by Goldschmidt's method, which consists in electrically heating a wire in the gas and from resistance measurements calculating the rate of conduction. A correction is introduced for loss of heat at the ends of the wire. The thermal conductivity of neon at the following temperatures is shown to be:  $105.9^\circ$ ,  $k' = 0.0001344$ ;  $0^\circ$ ,  $0.0001087$ ;  $-74.37^\circ$ ,  $0.0000879$ ; and  $-181.43^\circ$ ,  $0.0000499$ . These values are compared with the values calculated by means of the formula of Sutherland and a general formula of Maxwell. It is shown that, whilst there is good agreement in the second case, Sutherland's formula appears to be inapplicable at low temperatures. From a comparison of the thermal conductivities of argon, helium, and neon, it appears that the reduced thermal conductivity of neon changes in a different manner with the reduced temperature than the similar values for argon and helium. J. F. S.

**Empirical Formula for Calculating the Specific Heat of Water.** J. NARBUTT (*Physikal. Zeitsch.*, 1918, 19, 513—514).—The author has deduced an empirical formula for calculating the specific heat of water over the temperature range 0—100°. This formula is based on the experimental results of Ludin, Diesterici, Bousfield (A., 1911, ii, 580), Callendar (A., 1912, ii, 428), and Barnes and Cooke, and has the form  $c_t = 1.00733 - 0.0007416t + 0.000016845t^2 - 0.00000009552t^3$ , where  $c_{15} = 1$ . The agreement between the values calculated by this formula and the best experimental values are extremely good. J. F. S.

**Calculation of the Ratio of the Principal Specific Heats of Benzene and cyclohexane by Leduc's Cyclic Method.** G. DÉJARDIN (*Compt. rend.*, 1919, 168, 161—164).—Using Leduc's formula (compare *Ann. Physique*, 1915, [viii], 23, 577), the author finds that the value of  $\gamma$ , the ratio of the principal specific heats, for benzene at 20° is  $\gamma = 1.106$  and at 100°  $\gamma = 1.116$ , and for cyclohexane between 20° and 90° is  $\gamma = 1.077$ . Using the formula  $\gamma = 1 + 2/(\mu + \lambda)$ , where  $\mu$  is the number of degrees of liberty relative to the kinetic energy of the molecule and  $\lambda$  is the intramolecular potential energy, the author finds for benzene  $\gamma = 1.111$  and for cyclohexane  $\gamma = 1.083$  or 1.074, according as the degrees of liberty are taken as 24 or 27. W. G.

**Thermochemical Studies : Simplified Formula for Calculating the Molecular Latent Heat of Evaporation.** DANIEL LAGERLÖF (*J. pr. Chem.*, 1918, [ii], 98, 136—142).—Since all the author's calculated values and also Thomsen's experimental values for the heats of combustion of the hydrocarbons refer to the gaseous state, whilst most of the experimental values obtained by other authors refer to liquid or solid compounds, comparison of these different values requires a knowledge of the molecular latent heat of evaporation. The latter has been determined in but few cases, and can be derived only from Deprez and Trouton's law,  $q/T = \text{constant}$ . For the value of this constant, van't Hoff deduced the mean value 20.55 cal., whilst for non-associated liquids Kurbatov obtained the mean value 20.7 cal., the variation from the mean being at most 3—4%. From the equation

$$w_{\text{vap.}} = q = 20.55T$$

(or  $20.7T$ ), the author derives the expressions  $q = 0.02t + 5.6 + 0.00055t$  and  $q = 0.02t + 5.65 + 0.0007t$ , which refer to kilogram calories;  $t = T - 273$ . In order to arrive at an expression which may be easily remembered, he combines these two equations, with the result:  $q = w_{\text{vap.}} = 0.02t + 5.6 + 0.0007t$ . The third, variable member of the right-hand side may be neglected for values of  $t$  numerically less than 15°. The available experimental data show, however, that for uninuclear, aromatic hydrocarbons a fourth negative member must be introduced, the equation then becoming  $w_{\text{vap.}} = 0.02t + 5.6 + 0.0007t - (t - 80^\circ)/300$ . It is not known if cor-

rection is needed for multinuclear aromatic hydrocarbons, since no experimental numbers exist.

The values for the different terms of the above equations and the calculated and experimental values of  $w_{\text{vap}}$  are given in tabular form for a large number of hydrocarbons of different kinds. The differences between the calculated and experimental values are sometimes marked, but in most cases the agreement between them is extremely good.

T. H. P.

**Thermochemical Value of the Linkings Uniting the Atoms in Crystals.** M. PADOA (*Atti R. Accad. Lincei*, 1918, [v], 27, ii, 327-331).—If the union of the atoms in crystalline networks is affected by means of valency (compare this vol., ii, 51), a relationship should exist between the thermochemical data and the values of such linkings. Since the heat of combustion of diamond is 94.32 Cal. per gram-atom, and  $\text{CO} + \text{O} \rightarrow \text{CO}_2 + 68.22$  Cal., and since the thermochemical equivalence of the four valencies of carbon has been demonstrated, the difference  $94.32 - 68.22 = 26.10$  Cal. may be taken as the heat of formation of carbon monoxide from an atom of carbon combined in diamond, and the difference  $68.22 - 26.10 = 42.12$  as the heat of disintegration of the carbon atom, that is, the heat-equivalent of the energy required to dissolve the linking holding it in the crystal. From the structure of the diamond, it follows that with each carbon atom there correspond four half-valencies or two whole ones, so that each valency has the value  $42.12 : 2 = 21.06$  Cal. A similar value is obtained in the case of graphite.

Each free atom of carbon gives, then, on complete combustion,  $94.32 + 42.12 = 136.44$  Cal., and four free hydrogen atoms yield similarly four times the heat of combustion of a gram-atom of molecular hydrogen plus twice the heat of dissociation of the hydrogen molecule, that is,  $4 \times 34.35 + 2 \times 95 = 327.40$  Cal. Hence the sum  $136.44 + 327.40 = 463.84$  Cal., diminished by the observed heat of combustion of methane, namely, 212.70 Cal., gives 251.14 Cal., which constitutes the heat of formation of the methane molecule from its constituent free atoms; consequently, each C-H linking corresponds with  $251.14 : 4 = 62.78$  Cal. Similar calculation of the value of the C-C linkings in normal, saturated, open-chain hydrocarbons gives numbers varying from about 16 Cal. for the lower to about 18 Cal. for the higher members of the series.

In the case of benzene, which, according to Thomsen ("Thermochemistry," 1908, 393, 449), behaves thermochemically as if it contained nine simple linkings, and thus corresponds with the centric formula, each of these nine linkings represents a value of 16.6 Cal. With other cyclic hydrocarbons, increase in the number of nuclei is accompanied by increase in the mean number of linkings competing for each carbon atom, this number tending to the limiting value 2; at the same time, the mean value for each C-C linking increases towards the value, 21.0, for graphite. With hydrogenated hydrocarbons, such as cyclohexane, decahydronaphthalene, and *n*-octane.

the C-C values are somewhat higher than with the corresponding non-hydrogenated ones.

T. H. P.

**The Heat of Dissociation of Diatomic Gases in Relation to the Increase in the Value of  $\sqrt{a}$  of the Dissociated Atoms.** J. J. VAN LAAR (*Chem. Weekblad*, 1918, 15, 1124—1137).

—The theoretical considerations of this paper are based on the regularities observed by the author which are found to exist when the values of  $b$  and  $\sqrt{a}$  of the van der Waals's equation of state are brought into relation to the groups of the periodic system (A., 1916, ii, 386—387, 610; 1917, ii, 67). The values of  $b$  and  $\sqrt{a}$  for a compound are shown to be additive properties of the substance calculable from the values of the corresponding constants of the constituent elements. The value of  $b$  for any element is found to be independent of its state of combination, whether the element occurs free or combined in a molecule. On the other hand,  $\sqrt{a}$ , which is dependent on the mutual attraction of the molecules, is subject to variation according as the atom to which it relates is more or less shielded by other atoms in the molecule. For example, the values of  $\sqrt{a}$  for the carbon atom in  $\text{CH}_4$ , silicon in  $\text{SiH}_4$ , nitrogen in  $\text{NH}_3$ , are in each case found to be zero, that is, the central atom exerts no external attraction. In the case of hydrogen, nitrogen, oxygen, and the halogens, all of which dissociate into single atoms in suitable conditions of temperature, it has been found that  $\sqrt{a}$  is greatly increased in the monatomic state of the gas.  $\sqrt{a}$  thus becomes a measure of the "valency attraction" of the two atoms ( $\sqrt{A}$ ), whilst the value of  $\sqrt{a}$  ordinarily to be attributed to the same atom in compounds represents the "residual attraction." For carbon, the ratio of the two values is 32:31. Between the two constants  $\sqrt{A_K}$  and  $\sqrt{a_K}$  at the critical temperature, the following relation is established:

$$\sqrt{A_K} = \sqrt{a_K} \times \sqrt{(1 + \frac{1}{2}\theta Q_0/T_K)},$$

where  $Q_0$  is the energy liberated at  $T=0$  in the formation of one gram-molecule of gas from the free atoms,  $T_K$  is the critical temperature, and  $\theta$  a constant approximating to unity. The values of  $\sqrt{A}$  for various gases (hydrogen, nitrogen, oxygen, the halogens) calculated from this equation are in satisfactory agreement with the values which correspond with the position of these elements in the periodic arrangement.

W. S. M.

**The Effect of some Simple Electrolytes on the Temperature of Maximum Density of Water.** ROBERT WRIGHT (T., 1919, 115, 119—126).

**Compressibility of Aqueous Solutions, especially of Urethane, and the Polymerisation of Water.** THEODORE W. RICHARDS and SVEN PALITZSCH (*J. Amer. Chem. Soc.*, 1919, 41, 59—69).—The compressibility of water and of aqueous solu-

tions of urethane has been carried out by the method previously described (A., 1912, ii, 896). The concentration was varied from 0–56·01%, and the compressibility determined for pressures between 100–300 megabars. All experiments were conducted at 20°. In addition to these determinations, the solution volume, the surface tension, and the viscosity of urethane solutions were also determined. It is shown that with rising concentration, the compressibility decreases rapidly from  $43·25 \times 10^{-6}$  (the compressibility of pure water) to  $38·91 \times 10^{-6}$ , the compressibility of a solution of 34 grams of urethane in 100 grams of water. From this point, the compressibility increases, at first slowly and then more rapidly; at the highest measured concentration, 127·35 grams of urethane in 100 grams of water, the compressibility is  $40·86 \times 10^{-6}$ . The surface tension, specific volume, and viscosity showed no such minimum, and it is shown that none is to be expected. The results emphasise the theory of Whiting, which ascribes polymerisation to water.

J. F. S.

**Determination of the Compressibility of Solids at High Pressures.** LEASON H. ADAMS, ERSKINE D. WILLIAMSON, and JOHN JOHNSTON (*J. Amer. Chem. Soc.*, 1919, **41**, 12–42).—The compressibility of quartz, calcite, aluminium, sodium chloride, lead, brass, cadmium, zinc, tin, silver, copper, gold, bismuth, a tin-bismuth alloy, tool steel, and silica glass has been determined for pressures up to 12,000 megabars. The principle of the method employed is to compare the change of volume under pressure of a cylinder of the material with that of a similar cylinder of soft steel, the compressibility of which was considered to be  $0·60 \times 10^{-6}$  cm.<sup>3</sup>/megadyne. In carrying out the determination, the solid, surrounded by a liquid such as kerosene, was enclosed in a thick-walled steel bomb fitted with a movable non-leaking piston, and pairs of simultaneous readings were made of (1) the displacement of the piston, that is, the volume change, and (2) the pressure. The piston displacement was measured to 0·01 mm. by means of a dial micrometer. In measuring the pressure, advantage was taken of the change of resistance under pressure of a “therlo” wire, and in order to determine the pressure to within 1 megabar, the resistance was measured with a type of Wheatstone bridge having no movable contacts. The  $P\Delta v$  graph for gold, copper, brass, silver, aluminium, and calcite, like that of steel, is linear, but the graph for zinc, tin, cadmium, lead, the tin-bismuth alloy, quartz, bismuth, and sodium chloride shows an appreciable curvature, thus indicating for those substances a measurable decrease of compressibility with increasing pressure. A comparison was made of the compressibility of two alloys with that of their components. In the case of a simple mixture, such as the tin-bismuth alloy, the measurements indicate that the compressibility of mixtures the other properties of which, such as specific volume, electrical conductivity, and specific heat, are approximately linear functions of the composition, is related in the same

simple way to the compressibility of the separate components. On the other hand, the compressibility of alloys of the class to which brass belongs is much lower than the sum of the individual compressibilities.

J. F. S.

**Thermal Dissociation of Sulphur Dioxide.** J. B. FERGUSON (*J. Amer. Chem. Soc.*, 1919, **41**, 69—72. Compare this vol., ii, 15).—Starting from the equilibrium constant of the reaction  $\text{CO} + \frac{1}{2}\text{SO}_2 \rightleftharpoons \text{CO}_2 + \frac{1}{2}\text{S}_2$ , the author has calculated the degree of dissociation and the equilibrium constants of sulphur dioxide over the temperature range 1000—1500° and at pressures from 1 atm. to 0·001 atm. The degree of dissociation at 1500° and 1 atm. is found to be 5·9, whilst at 0·001 atm. it is 59. Consequently, it is obvious that the dissociation of sulphur dioxide is less than the dissociation of either carbon dioxide or water vapour.

J. F. S.

**Capillarity Constants of Pure Mercury and of Liquid Potassium Amalgam in Contact with Potassium Iodide Solutions.** V. POLARA (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 322—327).—Gouy (A., 1892, 760) showed that the capillarity constant of mercury in contact with aqueous potassium iodide solutions assumes a maximum value somewhat less than that of the same metal in contact with dilute sulphuric acid (1:6 by vol.). This behaviour is in contradiction to Lippmann's law, according to which the capillarity constant should be a function solely of the potential difference at the contact, and its maximum hence independent of the nature of the substances in contact. By means of Quincke's apparatus, the author has investigated the influence of the concentration of the potassium iodide on the maximum value of the capillarity constant of the mercury in contact with it and on the polarisation determining such maximum. Gradual increase of the concentration is found to be accompanied by progressive lowering in the maximum value of the capillarity constant, the difference for the two extreme cases ( $N/10$  and  $10N$ ) amounting to a variation of about 1 mm. in the difference of level between the two limbs of the apparatus; within the limits of sensitiveness of the method, the polarisation requisite for obtaining the maximum depression does not appear to be influenced by the concentration. Depression of the surface tension of the solution by addition of ethyl alcohol in various proportions produces marked lowering of the maximum of the capillarity constant, especially for percentages of the alcohol not exceeding 40; for higher proportions of alcohol, the effect is less pronounced. Also, potassium amalgams (2—0·1 part of potassium per 1000 of mercury) in contact with normal potassium iodide solution exhibit a capillarity constant which is somewhat lower than the maximum capillarity constant of pure mercury in contact with sulphuric acid solution, and diminishes sensibly with increase of the proportion of potassium dissolved in the mercury, the diminution being slower for the more concentrated than for the more dilute amalgams.

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Study of the variations in the density of the electric double layer at the contact with the polarisation by an apparatus detecting a change of 0.1 volt in the polarisation confirms the relation  $X = -dA/dp$ , where  $X$  is the density of the double layer,  $A$  the capillarity constant, and  $p$  the polarisation. This relation may be brought into accord with the circumstance that the capillarity constant does not depend solely on the potential difference at the contact by assuming that the function  $A$  has the form  $A = S - T(V - p)$ , where  $S$ , the ordinary surface tension, is independent of the potential difference at the contact, but depends, in agreement with the results obtained, on the particular conditions of the contact;  $T(V - p)$  is the symbol of a function only of the potential difference ( $V - p$ ) existing at the contact for each value of the polarisation employed ( $V$  = potential difference due to the contact and  $p$  the polarisation employed), and satisfying also the conditions  $dT/dp = X$  and  $(dT/dp)_{p=\pi} = 0$ . T. H. P.

**Velocity of Diffusion.** PHILIPP FRANK (*Physikal. Zeitsch.*, 1918, 19, 516—520).—A mathematical paper in which formulæ are deduced for the velocity of diffusion of gaseous molecules. The calculations are based on considerations of the Brownian movement, and are made in connexion with single particles and with the rate of advance of the "head" of a particle swarm.

J. F. S.

**Crystal Assemblage in Relation to the Atomic Field of the Crystal.** R. GROSS (*Jahrb. Radioaktiv. Elektronik.*, 1918, 15, 270—292).—The author uses the term "Sammelkrystallisation" (crystal assemblage) to signify the transformation of a substance from an amorphous or sub-crystalline to a distinctly crystalline state. A number of examples of the phenomenon are discussed. One of the most striking examples is a process used for making tungsten filaments. The finely divided metal, obtained by reduction of the oxide, is pressed into the form of wire and drawn slowly through a small heated coil at a temperature of 2000—2200°. When the rate of passage of the wire through the heated coil is properly regulated, it becomes converted into a single homogeneous, elongated crystal, the rate of growth of the crystal being equal to the rate at which the wire is travelling. The particles of tungsten of which the wire is originally composed have a mean diameter of about  $10^{-5}$  cm., and it has been shown by Debye (*A.*, 1917, ii, 574) by the X-ray method that this powder consists of cubic, crystalline particles. Other examples of crystal assemblage are afforded by the increase in size of the crystals of many metals by annealing, by the formation of silver crystals from a silver sol, and by the formation of calcite crystals when powdered calcium carbonate is heated under pressure. Some substances, for example, calcium sulphate, have a greater solubility than the normal when the particles in equilibrium with the solution are very small in size, but in course of time the solu-

bility falls to the normal owing to increase in the size of the particles. It is shown thermodynamically that the solubility should increase when the particles become very small, and it is concluded that the theory of minimum surface energy does not adequately explain crystal growth, since for very small particles the surface energy is not independent of the size. E. H. R.

**Liquid Crystals. II. Melting and Congelation Phenomena with *p*-Azoxyanisole.** W. J. H. MOLL and L. S. ORNSTEIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 254—258).—In a previous paper on the extinction of liquid crystals, it was suggested that two varieties of liquid crystals of *p*-azoxyanisole exist, ex-solid (produced by melting the solid) and ex-liquid (produced by cooling the isotropic liquid). To confirm this point, the authors have determined the fusion and congelation curves of *p*-azoxyanisole, and show from the results that there is no evidence from this source of the existence of two forms of liquid crystals of *p*-azoxyanisole. On the other hand, these curves show the existence of three solid forms of this substance: *p*-azoxyanisole I (m. p. 118°), *p*-azoxyanisole II (m. p. 104.5°), and *p*-azoxyanisole III (m. p. 116°). A fourth form, which melts at 108°, was shown to exist in the previous paper, but this form did not appear in the present work, and it is now shown only to be capable of existence in capillary layers (between gels). J. F. S.

**Molecular Mechanism of Colloidal Behaviour. I. The Swelling of Fibrin in Acids.** RICHARD C. TOLMAN and ALLEN E. STEARN (*J. Amer. Chem. Soc.*, 1918, **40**, 264—272).—The amount of swelling of blood fibrin in solutions of hydrochloric, nitric, sulphuric, acetic, and formic acids of various concentrations has been determined, as well as the amount of acid adsorbed by the fibrin from the solution. Similar experiments have been carried out with solutions of sodium chloride and with solutions of the above-named acids to which sodium chloride has been added. The data obtained are in accordance with the authors' theory of the molecular mechanism of protein swelling. This theory embraces the following points. On account of the amphoteric nature of protein colloids, they possess a marked tendency to adsorb hydrogen ions from acid solutions and hydroxyl ions from alkaline solutions. In an acid solution, the adsorbed hydrogen ions, together with an equivalent number of anions, form a "double layer" on the walls of the pockets or pores in the interior of the gel, and this leads to swelling and the imbibition of water by electrostatic repulsion. The addition of a strong electrolyte to such a swollen colloid, either a neutral salt or excess of the strong acid which caused the original swelling, will furnish ions in the interior of the pockets which will tend to arrange themselves so as to neutralise the electrical fields of the adsorbed layers, and thus bring about a reduction of the swelling. The addition of a neutral salt to an acid solution tends to neutralise the electrical field of



the adsorbed acid, and hence makes it easier for more acid to reach the surface of the pockets, thus leading to increased adsorption. Salts with multivalent ions should be more effective in reducing swelling than salts with univalent ions, since, for example, a bivalent ion will take up no more room than a univalent ion and will be twice as effective in neutralising an existing electric field. No assumptions are made as to the molecular nature of the adsorption of the hydrogen or hydroxyl ions; the theory would be equally tenable if the adsorption process should lead to a fairly uniform coating of ions over the whole of the exposed surface, or, on the other hand, if the hydrogen ion should only tend to go on to the protein molecule at special points where there is a particularly strong stray field, for example, where the amino- and acid groups of the amino-acids approach one another. J. F. S.

**Colours of Colloids.** WILDER D. BANCROFT (*J. physical Chem.*, 1918, **22**, 601—630).—A theoretical paper in which the author discusses the nature of the colour of natural objects. The subject is treated historically, and the various types of colouring individually treated. Colours are divided into two groups: (1) structural colours, and (2) pigmentary colours. The former group of colours owes its existence to the refraction, absorption, and interference of light. J. F. S.

**Degree of Dispersion of Colloids and its Determination.** GEORGE KING (*J. Soc. Chem. Ind.*, 1919, **38**, 4—7T).—A short account is given of the slit ultra-microscope and its capabilities. In counting the number of colloidal particles in a definite volume of colloidal solution, it is necessary, owing to the rapid Brownian movement, to take the mean of the numbers of particles observed at ten momentary observations, and the solutions should be diluted with colloid-free medium until there are never more than four particles in the field at the same time. The periodic illumination may be effected by allowing a pendulum screen to swing in front of the micrometer slit, the impression of the number of particles seen being then very definite. The solution in the observation cell should be changed at least ten times, and the mean of the one hundred separate counts taken; further, one or more controls with fresh dilution should always be made.

The paraboloid, Leitz, and Cotton and Mouton devices for dark-ground illuminations serve well for qualitative observation, but are useful only for coarse hydrosols; they are, moreover, unsuitable for the rapid examination of colloidal solutions, as the adjustment of the instrument must be disturbed for each small quantity observed and a fresh volume of solution introduced into the special microscope slide. With the cardioid ultra-microscope, it is possible to distinguish particles beyond the range of the old slit ultra-microscope, owing to the fact that the hydrosol can be more intensely illuminated. The slit ultra-microscope has now been enhanced in sensitiveness by using objectives of high numerical

aperture (1.05), one at right angles to the other, the front lenses, made of quartz, being both immersed in the hydrosol. By this means, the size of the particles which can be counted is diminished from  $5\mu$  to  $3\mu$ , whilst even smaller particles can be seen in concentrated solution, but not accurately counted in dilute solution.

With the new immersion ultra-microscope, qualitative examinations were made of solutions of peptone, starch, gelatin, agar-agar, and dextrin in the concentrations used by Findlay and King (T., 1913, 1170; 1914, 1297), but these were found to be optically clear under the best conditions for illumination, etc.; the refractive indices of the medium and colloid are doubtless nearly equal. Merck's ferric hydroxide is, however, countable.

Of physiological interest is the condition of casein in cow's milk and human milk. The particles in the latter are uncountable in the slit ultra-microscope, but they can be counted in the new instrument, whilst casein in cow's milk is easily seen in the slit ultra-microscope. Thus it would seem that, when it is to be used for feeding infants, cow's milk should be so treated as to cause an increase in the degree of dispersion of the casein particles; this is not effected by mere dilution of the milk.

When it is necessary to determine the size of microscopic particles in a suspension, use may be made of Stokes's formula,  $V = F/6\pi\eta r$ , where  $V$  = velocity of fall,  $F$  = force acting,  $\eta$  = viscosity, and  $r$  = radius of particle. Other methods which have been used are discussed by Henri (*Trans. Faraday Soc.*, 1918, 47), but are not convenient for technical application.

T. H. P.

**The System Iron-Oxygen.** A. SMITS and J. M. BLIJVOET (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, 21, 386—400).—A theoretical paper in which the three-phase systems  $\text{FeO}, \text{Fe}, \text{gas}$  and  $\text{Fe}_3\text{O}_4, \text{FeO}, \text{gas}$  are considered. The gas in question is either of the reducing mixtures  $\text{CO}_2, \text{CO}$ , or  $\text{H}_2\text{O}, \text{H}$ . On the basis of the deductions drawn from the above-mentioned considerations, the processes operative in the blast furnace are theoretically investigated. The  $P.T.$  diagram of the system oxygen-iron is derived from the equilibria of the iron oxides in reducing and oxidising gases respectively. Calculations are made of the oxygen dissociation tension, and these values, as was to be expected, are very small.

J. F. S.

**Influence of Temperature on Homogeneous Gas Reactions.** GEORGE W. TODD and S. P. OWEN (*Phil. Mag.*, 1919, [vi], 37, 224—230).—A mathematical paper in which from Maxwell's distribution theorem an expression has been deduced by which the number of molecules having a velocity greater than a particular value may be calculated. This expression has the form

$$n = 2Ne^{-x^2} / \sqrt{\pi(x_1 + \frac{1}{2}x_1)},$$

in which  $n$  is the number of molecules per c.c. which have a velocity greater than  $c$ , and  $x = c\sqrt{m/2R\theta}$ ; all the other factors have their usual significance. Assuming that only molecules with kinetic

energies greater than a definite minimum have the power to react with other molecules, it is shown how the velocity constant of a gaseous reaction varies with temperature. This is represented for the general case by the equation

$$k_{\theta_2}/k_{\theta_1} = \phi\theta_2/\phi\theta_1(e^{W(1/\theta_1 - 1/\theta_2)}),$$

in which  $W$  is a constant. The general relationship for the dependence of the equilibrium constant on the temperature is also deduced.

J. F. S.

**The Evolution and Magnetic Properties of Chromic Hydroxide in Alkaline Solution.** F. BOURION and A. SÉNÉCHAL (*Compt. rend.*, 1919, 168, 89—91. Compare this vol., ii, 66).—The velocity constants for the rate of oxidation of chromic hydroxide in alkaline solution by hydrogen peroxide at 17° and 30° during the first eight hours correspond fairly well with those for a quadrimolecular reaction. The paramagnetism of an alkaline solution of chromic hydroxide diminishes slowly with time, but the diminution is small and never exceeds 20%.

W. G.

**Polar and Non-polar Valency.** RAJENDRALAL DE (T., 1919, 115, 127—134).

**Automatic Variation of Gas Pressure and its Application to a Vacuum Pump, Circulation of Gases [and] Magnetic Stirrer.** O. MAASS (*J. Amer. Chem. Soc.*, 1919, 41, 53—59).—An apparatus is described which, when attached to a Toepler mercury pump, may be used for the periodic variation of gas pressure. By suitable adjustments, which are described in the paper, the apparatus may be employed for the circulation of gases and for working a magnetic stirrer.

J. F. S.

## Inorganic Chemistry.

**Determination of the Rate of Solution of Atmospheric Nitrogen and Oxygen by Water.** I. W. E. ADENEY and H. G. BECKER (*Sci. Proc. Roy. Dubl. Soc.*, 1918, 15, 385—404).—The rate of solution of nitrogen and oxygen in distilled water, tap-water, and sea-water has been determined at temperatures between 11.3° and 12.3° by allowing a bubble of the air to pass up a narrow glass tube containing the water. This affects the mixing of the solution and constantly exposes the air to a fresh surface of water. The object of the experiments was to substantiate the authors' views on the mechanism of solution of a gas in the liquid. Contrary to the generally accepted view, it is held that the gas is

absorbed by the surface layer, but the gases do not remain concentrated here; they are gravitationally drawn downwards through the lower layers of water with comparative rapidity (compare *ibid.*, 1914).  
J. F. S.

**Flame Reactions: Selenium and Tellurium in the Hydrogen-Air Flame.** JACOB PAPISH (*J. physical Chem.*, 1918, 22, 640—646).—The elements selenium and tellurium, as well as their dioxides and hydrides, have been introduced into the hydrogen air flame and the colour changes observed. At the same time, experiments were made to ascertain the nature of the deposit, if any, on a cold object introduced into the flame. Selenium dioxide produces a deep blue luminescence in the inner zone, pale blue in the middle zone, and green in the outer zone. There was a deposition of selenium in the inner and middle zones, but no deposition in the outer zone. Hydrogen selenide produces a very faint blue luminescence in the inner zone, deep blue in the middle zone, and green in the outer zone. There was a deposition of selenium in the inner zone, but no deposition elsewhere. Selenium produces a luminescence coloured blue, violet, and green in the inner, middle, and outer zones respectively; in this case and in all following cases, the element was deposited in the inner and middle zones, but there was no deposition in the outer zone. Tellurium dioxide, hydrogen telluride, and tellurium all produce a lilac luminescence in the middle zone and a green luminescence in the outer zone, whilst tellurium dioxide and the free element produce a green luminescence in the inner zone, whereas the hydrogen telluride produces a blue luminescence in this region. Possible explanations for the differences in the various cases are suggested.  
J. F. S.

**The Constitution of Nitrous Vapours.** P. JOLIBOIS and A. SANFOURCHE (*Compt. rend.*, 1919, 168, 235—237).—When nitric oxide and oxygen are mixed at the ordinary temperature in the proportion of 4:1 by volume, combination is instantaneous, and nitrogen trioxide is formed and remains unchanged. If the gases are mixed in the proportion of 2:1, or if an excess of oxygen is used, the combination rapidly reaches the stage of the trioxide, but after twenty seconds 34% of the peroxide is formed, after thirty-seven seconds 68%, and after 100 seconds 92%. If nitrous vapours are heated at 400°, the equilibrium tends towards the formation of the trioxide, with partial destruction of the nitrous vapours.  
W. G.

**The Synthesis of Ammonia at High Temperatures. III.** EDWARD BRADFORD MAXTED (*T.*, 1919, 115, 113—119).

**Production of Ammonia from "Nitrolime," and the Time Yield under Various Conditions.** WERNER GRAHMANN (*Zeitsch. Elektrochem.*, 1918, 24, 385—391).—The rate of produc-

tion of ammonia from boiling mixtures of "nitrolime" and water, "nitrolime" and sodium hydroxide or sodium carbonate of various concentrations, and "nitrolime" and potassium hydroxide or carbonate of various concentrations has been determined. In the case of "nitrolime" and water, it is shown that the rate of decomposition of calcium cyanamide is extremely slow in all concentrations at the boiling point and atmospheric pressure. Thus a 1% solution is decomposed to the extent of 98% by seventy-two hours' boiling. In the presence of sodium carbonate, the decomposition really amounts to the decomposition of sodium cyanamide (*a*) under a constant sodium hydroxide concentration, and (*b*) under a concentration of sodium hydroxide, which increases during the reaction. In the case of an addition of sodium hydroxide, the decomposition takes place under a regularly increasing concentration of the hydroxide. The same remarks apply to the decompositions in the presence of potassium carbonate and hydroxide. The presence of alkali hydroxide or alkali carbonate has an accelerating influence on the reaction; the velocity increases with increasing concentration of the added salt to a maximum, after which it remains more or less constant. The maximum in the case of alkali hydroxides occurs with much lower initial concentration of alkali than in the case of the alkali carbonates, for in these experiments the alkali concentration increases continuously from beginning to end of the decomposition. The experiments with potassium hydroxide and carbonate do not show the same maximum as the sodium compounds under similar conditions, so that, since sodium hydroxide and potassium hydroxide are ionised to practically the same extent, it must be taken that the acceleration of the decomposition velocity is not dependent entirely on the hydroxyl-ion concentration, but that the cation and the undissociated molecules also exert a specific action. A number of orientating experiments were carried out under 30 atmospheres pressure at 150°. Under these conditions, it is shown that, even without the addition of alkali, the decomposition takes place very rapidly until 75% of the calcium cyanamide is decomposed, after which the velocity becomes much less, thus: in an aqueous solution 75% is decomposed in forty-five minutes, but only 90% is decomposed in 120 minutes. In the presence of 10% alkali hydroxide, 75% decomposition is reached in thirty minutes and 90% in seventy-five minutes. The "nitrolime" used in the experiments contained 16.85% of cyanamide nitrogen, 0.65% of dicyanodiamide nitrogen, 22.30% free lime, and 0.31% sulphur.

J. F. S.

**Effect of Phosphine and Hydrogen Sulphide on the Oxidation of Ammonia to Nitric Acid.** GUY B. TAYLOR and JULIAN H. CAPPS (*J. Ind. Eng. Chem.*, 1919, 11, 27—28).—Pure acetylene has no effect on the catalytic oxidation of ammonia to nitric acid in presence of platinum (compare A., 1918, ii, 265). The opposite results obtained earlier being due to the fact that the acetylene used contained small proportions of phosphine.

Hydrogen sulphide in low concentrations has no immediate toxic effect on the catalytic oxidation. [See *J. Soc. Chem. Ind.*, March.]

T. H. P.

**Oxidation of Coal.** J. R. PARTINGTON (*Chem. News*, 1919, 118, 50—51).—The experimental results obtained by Wheeler (T., 1918, 113, 945) are discussed, and an alternative explanation offered. The assumption that air is absorbed by freshly won coal with formation of an additive compound, such as a complex oxide, is an improbable one. The facts agree better with the hypothesis that the process is one of adsorption, followed by direct formation of carbon monoxide. Carbon dioxide may be produced by oxidation of the carbon monoxide by moisture, or even by interaction of carbon and water, hydrogen being formed at the same time. The adsorption hypothesis explains the differences observed when moist or dry air is used. In absence of moisture, the proportion of carbon dioxide formed would be expected to be lower than when moisture is present. The fall of the ratio  $\text{CO}_2/\text{CO}$  with rise of temperature also follows from the adsorption hypothesis.

E. H. R.

**The Interaction of Stannous and Arsenious Chlorides.** REGINALD GRAHAM DURRANT (T., 1919, 115, 134—143).

**Stable Solution of Silver Nitrate.** F. LIEBERT (*Chem. Weekblad*, 1919, 16, 74).—The solution of the salt is exposed to the light until the organic matter present is exhausted, and is then filtered through asbestos. The resulting solution may be kept in light without further alteration.

W. S. M.

**Atomic Weight of Lead from Samarskite.** ARTHUR L. DAVIS (*J. Physical Chem.*, 1918, 22, 631—639).—Using a specimen of lead obtained from samarskite which contained  $\text{U}_3\text{O}_8$  12.21% and  $\text{ThO}_2$  1.03%, the author has determined the atomic weight of this element. The method adopted was that of Baxter and Grover (A., 1915, ii, 456), and consisted in converting lead chloride into silver chloride. In three experiments, results varying from 206.246 to 206.363 were obtained for the atomic weight of lead. Calculations made from the content of samarskite on thorium and uranium lead to a value of 206.06 for the lead contained in this mineral, whereas the experimental value is 206.30. This corresponds with a mixture of 3 parts of radio-lead and 1 part of ordinary lead. If it is assumed that 8% of the uranium is transformed along the actinium series to form a stable isotope of atomic weight 210, the value 206.38 is calculated for the atomic weight of samarskite lead. The experimental value, however, is in better agreement with the supposition that either or both of the isotopes of lead in the thorium series are relatively short-lived, and that the lead in samarskite represents a mixture of radio-lead of the uranium series, atomic weight 206, and radio-lead of the actinium

series, atomic weight 210. This conclusion is not in agreement with the value 206.04 found by Hönigschmidt for the atomic weight of lead from crystallised uraninite (A., 1914, ii, 553).

J. F. S.

**The Sub-acetate and Sub-sulphate of Lead.** HENRY GEORGE DENHAM (T., 1919, 115, 109—113).

**The Rusting of Iron on Contact with other Metals and Alloys.** O. BAUER and O. VOGEL (*Mitt. k. Materialsprüf.*, 1918, 36, 114—208).—A discussion of previous work and new experiments on the influence of other metals on the corrosion of iron in conductivity water, distilled water, and chiefly 1% sodium chloride solution. Much attention is paid to the potential difference between the metals and electrolyte, which was measured as follows: the cell, together with a millivoltmeter and a resistance of 100,000 ohms, is placed in parallel with a standard resistance,  $W$ . A small current,  $i$ , is passed, which is adjusted until no deflection of the galvanometer is obtained, when the potential difference  $= iW$ . A large number of results are given for the potential difference of pure metals and graphite against the normal calomel electrode. The contact of two metals in the 1% salt solution results in a large increase in the corrosion of the more electro-negative metal, that of the more electro-positive one being reduced. In the water this effect is much less marked. Rusting of iron is entirely prevented when a current was passed which counterbalanced the solution pressure in the electrolyte, so rendering the passage of the ions into solution impossible. For electrolytic iron in 1% sodium chloride solution at 18°, a minimum current density of 0.0000106 amps. per sq. cm. is required, calculated from the formula  $(a.F)/(Fe/2.qs)$ , where  $a$  is the loss of weight of the iron in grams,  $F$  96,540 coulombs,  $Fe/2$  half the atomic weight of iron,  $q$  surface of iron in sq. cm. exposed to attack, and  $s$  duration of corrosion in seconds. [See, further, *J. Soc. Chem. Ind.*, March.]

F. C. TH.

**Investigation of the Crystal Structure of White and Grey Tin by means of X-Rays.** A. J. BIJL and N. H. KOLKMEIJER (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, 21, 405—408).—The structure of the two allotropic modifications of tin has been investigated by means of X-rays. The method adopted was that due to Debye and Scherrer, and the interference photographs obtained indicate that both forms of the metal are crystalline.

J. F. S.

**Reduction of Osmium Tetroxide by Hydrogen Chloride.** OTTO RUFF and SUSANNE MUGDAN (*J. pr. Chem.*, 1918, [ii], 98, 143—144).—The conclusion drawn by Milbauer (A., 1918, ii, 202) that osmium tetroxide is reduced to osmium monoxide by hydrochloric acid is opposed to the results obtained by Ruff and Bornemann (A., 1910, ii, 305) and by Ruff and Rathsburg (A., 1917,

ii, 323), and repetition of Milbauer's experiments by the authors shows that the tetroxide undergoes reduction to a slight extent to the dioxide, but not to the monoxide; the bulk of the tetroxide remains unchanged in the hydrochloric acid solution. Milbauer's erroneous results appear to be due to the presence in the tetroxide of impurities, although the commonest of these, namely, ruthenium tetroxide, behaves similarly to osmium tetroxide. T. H. P.

### Mineralogical Chemistry.

**Fibrous Quartz from Rhode Island.** ALFRED C. HAWKINS (*Amer. Min.*, 1918, **3**, 149—151).—Fibrous quartz resembling asbestos in appearance, and consisting of long, delicate, flexible fibres, fills narrow veins in metamorphic slates at several localities in Rhode Island. It ranges in colour from pure white to green. The green colour is due to the presence of admixed actinolite, as shown by microscopical examination and by the following analyses: I, green from Fenner's Ledge, Cranston; II, white from the same locality; III, green from Portsmouth.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	H <sub>2</sub> O.	CO <sub>2</sub> .	S.	Total.
I. 77-15		8.72	7.68	0.70	3.96	1.40	—	0.52	100.13
II. 94-92		4.56		trace	trace	0.16	—	—	99.64
III. 91-83		1.61	3.81	0.80	1.37	0.70	0.50	0.12	100.74

L. J. S.

**Hambergite from Kashmir.** R. C. BURTON (*Rec. Geol. Survey India*, 1913, **43**, 168—172).—Crystals of hambergite, together with cookeite, prehnite, tourmaline, beryl, euclase (?), and amblygonite, have been found in the granitic debris in the Kashmir sapphire mines. They were probably derived from the neighbouring pegmatites. A description is given of a twinned crystal. Analysis gave:

GIO.	B <sub>2</sub> O <sub>3</sub> .	H <sub>2</sub> O.	Total.	Sp. gr.
52.40	[37.39]	10.21	100.00	2.36

L. J. S.

**Phosphorite from the Island of Juan de Nova, Madagascar.** J. ORCEL (*Bull. Soc. franç. Min.*, 1918, **41**, 104—108).—The phosphate deposits on the small island of Juan de Nova, or St. Christophe, about eighty miles off the west coast of Madagascar, have been formed by the action of soluble phosphates, derived from guano, on the underlying coral-rock. Analysis I is of brown, concretionary phosphorite, and II of brown, earthy material of prac-



tically the same composition. The latter is worked under the name "leached guano." The analysis (I) shows an excess of 8.45% CaO, indicating the voelckerite formula  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaO}$  (A., 1912, ii, 565).

	CaO.	SrO.	MgO.	Al <sub>2</sub> O <sub>3</sub> .	P <sub>2</sub> O <sub>5</sub> .	Cl.	SO <sub>3</sub> .
I.	48.63	0.17	1.75	0.15	35.56	0.29	0.56
II.	46.85		n.d.	0.38	35.19	0.14	0.58
	CO <sub>2</sub> .	Organic matter.	H <sub>2</sub> O.	Loss at 110°.	Insol.	Total.	
I.	0.14	1.27	7.97	4.00	0.05	100.54	
II.	10.08			5.32	0.03	98.57	

L. J. S.

**The Colour Change in Vivianite.** THOMAS L. WATSON (*Amer. Min.*, 1918, 3, 159—161).—The large, pale green crystals of vivianite from Plant City, Florida (A., 1918, ii, 119), are non-pleochroic and yield a colourless powder. This powder rapidly changes, especially in sunlight, to deep blue, and becomes strongly pleochroic. An unground sample of the crystals showed FeO 42.88%, whilst the finely ground material gave FeO 38.43%. The change in colour and pleochroism is thus due to the partial oxidation of the iron, and not to inversion as was at first suggested by the microscopical aspect of the material. A tabulation of the refractive indices of pale green and of dark blue vivianite from various localities indicates that the oxidation has been accompanied by an increase in the values of  $\beta$  and  $\gamma$ .

L. J. S.

**Copiapite in Coal.** WILLIAM J. MCCAUGHY (*Amer. Min.*, 1918, 3, 162—163).—A specimen of pale green, fibrous melanterite from the Congo coal mine in Perry County, Ohio, changed in the course of a year to dull white, and the fibres became brittle. Yellow spots also developed, especially at the points of contact between the melanterite and the associated shale. This yellow material consists of minute, tabular crystals, and is proved by the following analysis and refractive indices to be copiapite,  $\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 18\text{H}_2\text{O}$ .

SO <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	H <sub>2</sub> O.	Insol.	Total.	$\alpha$ .	$\beta$ .	$\gamma$ .
39.68	29.98	30.45	0.31	100.42	1.525	1.545	1.595

L. J. S.

**Nasonite from Långban, Sweden.** G. AMINOFF (*Geol. Förh.*, 1916, 38, 473).—This mineral, hitherto known only from Franklin, New Jersey (A., 1900, ii, 89), has been observed at Långban in the veins of "secondary calcite," where it is associated with schefferite, native lead, apophyllite, etc. It forms white to pearl-grey lamellar masses, or, less often, hexagonal prisms with

rounded faces. Refractive indices (Na),  $\omega=1.9453$ ,  $\epsilon=1.9710$ . Analysis by R. MAUZELIUS agrees with the usual formula  $Pb_1(PbCl)_2Ca_4(Si_2O_7)_3$ .

SiO <sub>2</sub>	PbO.	FeO.	MnO.	CaO.	MgO.	Cl.	H <sub>2</sub> O.	Total.
18.23	67.67	0.04	0.14	11.29	0.20	2.90	0.24	100.71

L. J. S.

**Anorthite from Japan.** S. KÖZU (*Sci. Rep. Tohoku Imp. Univ.*, 1914, Geol. Ser., 2, 7—33).—The results are given of elaborate determinations of the optical constants (refractive indices, optic axial angle, and dispersion of the optic axes) for different wavelengths of anorthite from three Japanese localities. As these show certain differences amongst themselves, the following analyses, by H. S. WASHINGTON, were made of I, anorthite crystals from Miyake-jima, one of the Seven Izu Islands south of Tokyo, and II, crystals from the Tarumae volcano in Hokkaidō.

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	Total.	Sp. gr.
I. 44.49	36.00	0.08	19.49	0.04	0.03	0.59	100.72	2.758
II. 44.03	35.93	0.10	18.66	trace	0.07	1.00	100.24	2.757

Barium and strontium are absent, and the slight differences in composition cannot be correlated with the differences in the optical constants. I corresponds with  $Ab_{3.9}An_{95.4}Cg_{0.7}$  and II with  $Ab_{4.7}An_{92.6}Cg_{2.7}Or_{0.6}$ . The melting points are 1538° and 1536° $\pm 2^\circ$  respectively.

L. J. S.

**Racewinite, a New Mineral from Utah.** A. N. WINCHELL (*Econ. Geol.*, 1918, 13, 611—615).—The mineral occurs as veins and irregular masses in limestone, and also replacing the carbonate portion of calcareous sandstones, near the contact with porphyry in the Highland Boy mine at Bingham, Utah, where it is often intergrown with pyrites and other ore minerals. It is brownish-black with a dull to bright lustre, and somewhat resembles coal in appearance. When freshly taken from the mine, it is bluish-green; the change in colour to brownish-black takes place slowly throughout the whole mass, and after six months the largest pieces were altered to the centre. The mineral undergoes other remarkable changes in colour. In boiling nitric acid it is insoluble, but gradually changes to yellowish-brown and translucent. In hydrochloric acid, it is slowly soluble and shows the same change in colour. Thin splinters and particles under the microscope are pale to brownish-yellow. In clove-oil this colour changes first to grass-green and then to black, but the same change does not take place in cedar-oil and some other oils. The finely powdered mineral is nearly white with a yellow tinge. The material is coarsely crystalline with no cleavage or crystal-faces; it is friable and the fracture conchoidal. Sp. gr. 1.94—1.98, H 2½; optically biaxial with large angle and negative,  $n$  about 1.51. It adheres to the tongue and slakes in water, breaking up with a sharp, audible

sound. Analyses I and II by J. P. HICKEY and C. L. AUSTIN respectively:

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	H <sub>2</sub> O.	Total.
I. 43-92	23-68	7-37	2-52	0-50	22-04	100-03	
II. 43-24	23-69	8-05	2-42	0-78	21-80	99-98	

A sample of the green, unaltered mineral showed 0-60% FeO. Over sulphuric acid, 7-8% H<sub>2</sub>O is lost in one day and 14% after forty-nine days; this is re-absorbed from a moist atmosphere. Other determinations gave the loss at 70° as 8% and at 200° as 12-1%. Heated to dull redness, the crystal structure is not destroyed, and the optical characters are not materially altered.

L. J. S.

**New Swedish Minerals.** GUST. FLINK (*Geol. För. Förh.*, 1917, 39, 426-452).—*Ektopite* forms crusts of small, brown, rectangular plates on garnet with calcite and barytes in magnetite ore from the Norrbotten mine at Långban. The crystals are monoclinic ( $a:b:c=0.74:1:0.84$ ,  $\beta=61^{\circ}5'$ ) with a tabular habit parallel to the orthopinacoid and elongated in the direction of the axis of symmetry. They are opaque with a vitreous to silky lustre, but in thin splinters under the microscope, the material is translucent and yellow. D 2.46, H 4,  $n$  1.62—1.63. Analysis I, by N. SAHLBOM, gives the formula  $12\text{RO}, 8\text{SiO}_3, 7\text{H}_2\text{O}$ . The mineral is related to caryopilitite and neotocite.

	SiO <sub>2</sub> .	Sb <sub>2</sub> O <sub>5</sub> .	PbO.	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.
I. 35-02	—	—	—	0.75	—	5.80
II. 7-75	20-76	—	—	9.50	3.58	2.44
III. 34-72	—	—	41.74	—	—	—

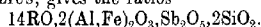
  

	MnO.	CaO.	MgO.	H <sub>2</sub> O.	Total.
I. 37-20	3.59	7.20	8.89	99.89*	
II. 52-61	0.53	3.06	0.11	100.39	
III. 2-17	20.28	0.20	0.10	99.90†	

\* Including K<sub>2</sub>O 1.13, Na<sub>2</sub>O 0.12, metallic sulphides 0.19.

† Including BaO 0.69.

*Katoptrite* occurs as tabular crystals and irregular lumps with magnetite in granular limestone in the Brattfors mine at Nordmark. The crystals are monoclinic ( $a:b:c=0.79223:1:0.48985$ ,  $\beta=78^{\circ}57'$ ) and have a highly perfect cleavage parallel to the orthopinacoid  $a(100)$ . This cleavage resembles that of mica, but the cleavage flakes are very brittle and not flexible. D 4.5, H 5½. The mineral is black and opaque with a bright metallic lustre. Thin flakes are red by transmitted light and strongly pleochroic. Analysis II, by R. MAUZELIUS, gives the ratios



The mineral resembles manganostibite in appearance, and it may perhaps be identical with the incompletely described hematostibite.

*Margarosanite* (A., 1916, ii, 532).—This new mineral has been found in some quantity in the "Lukas Ort" and Bjelkes shaft at Långban, where it is associated with nasonite, schefferite, apo-

phyllite, calcite, etc. The masses, weighing up to 1 kilo., are snow-white with pearly lustre and columnar structure. Crystals are rare; these are triclinic ( $a:b:c=0.74998:1:1.2849$ ,  $\alpha=74^\circ 37'$ ,  $\beta=50^\circ 28'$ ,  $\gamma=78^\circ 53'$ ) with three cleavages, that in one direction being highly perfect. D 4.39, H 2½. Analysis III, by R. MAUZELIUS, gives the formula  $\text{PbCa}_2(\text{SiO}_3)_3$ . The mineral is readily and completely soluble in dilute nitric acid. It is perhaps a member of the pyroxene group.

Thaumasite from Langban is described as loose aggregates of small but distinct crystals. These are hexagonal with prismatic habit,  $a:c=1:0.9479$ . L. J. S.

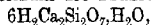
**Minerals in the Crystalline Limestone of Crestmore, California.** ARTHUR S. EAKLE (*Bull. Dep. Geol. Univ. California*, 1917, 10, 327–360).—At Crestmore, in Riverside County, two hills of crystalline limestone, resting on a boss of granodiorite and intruded by veins of quartz-monzonite-porphry and pegmatite, are extensively quarried for the manufacture of Portland cement, the partly decomposed granodiorite (anal. I) being used as a substitute for clay. In one hill the limestone is a white marble (anal. II), whilst in the other it is composed largely of blue calcite. In the latter, the metamorphic processes have been more intense, there having also been hydrothermal action by phosphatic, siliceous, and carbonated solutions, and zones composed of a great variety of metamorphic minerals have been developed at the contacts with the intrusive veins. The blue calcite, which forms bands and patches intermixed with the metamorphic minerals, is sometimes of a deep colour, fading on exposure to sky-blue. It is decolourised at a low heat, and the colour is thus perhaps due to organic matter. Detailed descriptions are given of about fifty mineral species from this locality, and analyses of the following. Wilkeite (A., 1914, ii, 283) and xanthophyllite (A., 1916, ii, 443) have been previously described.

Brucite (anal. III) forms grey, yellow, or red granules embedded in the white limestone. It consists of an aggregate of twisted plates and threads much compressed and strained, and has no doubt been derived from periclase ( $\text{MgO}$ ) with an accompanying considerable ( $2\frac{1}{2}$  times) increase in volume. Wollastonite is of abundant occurrence as columnar and fibrous masses; as snow-white, finely granular and loosely coherent aggregates (anal. IV); and as crystals of various types (anal. V of clear crystals). The distribution of the faces on these crystals indicates that the symmetry is monoclinic-hemimorphic, or perhaps triclinic. Several new crystal-forms are noted. The mineral is strongly triboluminescent. Refractive indices,  $\alpha=1.614$ ,  $\beta=1.629$ ,  $\gamma=1.631$ . Idocrase as yellow or brown crystals and masses is also abundant; anal. VI, by J. B. WRIGHT, of green idocrase. Garnet, crystals and massive, of a cinnamon colour occurs with the idocrase; anal. VII by J. B. WRIGHT, of massive grossularite. A new analysis (VIII by

G. SURR) is given of the monticellite which occurs in intimate association with the xanthophyllite.

Two new species, *crestmoreite* and *riversideite*, hydrated calcium silicates, are described. *Crestmoreite* is an alteration product of wilkeite, and in the description of this mineral it was provisionally referred to as *okenite* (A., 1914, ii, 283). It occurs as small patches of earthy to compact, snow-white, and opaque material in the blue calcite. Under the microscope, it shows straight extinction with positive elongation, low birefringence, and  $\beta=1.590$ . Hardness 3. It is readily soluble in acid with separation of some flocculent silica, although most of the silica goes into solution. Boiling water extracts some calcium. Water is expelled mostly at a high temperature; at  $200^{\circ}$  the loss is 3.27%, and at  $300^{\circ}$  10.27%. From the analyses IXa—c, a complex formula is deduced, but the phosphate, sulphate, and carbonate no doubt represent admixed unaltered wilkeite. Simpler formulae are  $\text{CaSiO}_3 \cdot \text{H}_2\text{O}$  and  $4\text{H}_2\text{CaSiO}_4 \cdot 2\text{H}_2\text{O}$ , preference being apparently given to the former.

*Riversideite* occurs as narrow seams of white, fibrous material in massive idocrase.  $H=3$ ; refractive indices,  $\alpha=1.595$ ,  $\gamma=1.603$ ; the fibres give straight extinction with positive elongation. A complex formula is deduced from anal. X; neglecting phosphate and sulphate, simpler formulae are  $2\text{CaSiO}_3 \cdot \text{H}_2\text{O}$  and



preference being given to the former. These two new minerals may be regarded as hydro-wollastonites.

Orthoclase, pure white material from the pegmatite, anal. XI. Okenite (anal. XII, by W. FOSHAG) occurs as tufts of long, slender needles and fibres on apophyllite, which is found in cavities in wollastonite between the pegmatites and the limestone. The crystals are probably orthorhombic,  $n=1.55$ . Prehnite occurs in cavities in the felspar of the pegmatites; in addition to the usual green drusy type, there is also a pale brown to colourless type, which forms crystals or, more often, compact, granular masses. Anal. XIII of the brown prehnite. Laumontite (anal. XIV) as columnar and fibrous masses occurs on the green prehnite.

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{FeO}$	$\text{CaO}$	$\text{MgO}$	$\text{P}_2\text{O}_5$	$\text{SO}_3$	$\text{CO}_2$	$\text{H}_2\text{O}$	Total	Sp. g.
I.	60.60	16.61	5.03	—	7.03	2.08	—	—	4.79	—	97.08*	—
II.	4.15	1.29	—	—	50.78	2.50	—	—	40.60	—	99.58	—
III.	—	—	0.55	—	—	67.48	—	—	—	31.73	99.76	2.39
IV.	51.77	—	3.12	—	44.85	—	—	—	—	1.02	99.76	—
V.	50.42	—	0.51	—	48.29	0.80	—	—	—	0.07	99.80	—
VI.	39.68	17.61	3.11	0.46	38.27	4.73	—	—	0.61	99.67†	99.67	3.36
VII.	35.53	21.11	3.95	5.0	38.06	0.78	—	—	1.23	100.15‡	99.89	—
VIII.	37.46	—	—	3.44	35.14	25.32	—	—	—	100.86	99.77	—
IXa.	36.12	—	—	—	42.71	—	2.38	2.42	1.16	14.98	99.42	—
IXb.	38.30	—	—	—	41.20	—	3.50	1.25	—	15.17	99.42	—
IXc.	34.42	—	—	—	43.54	—	3.50	2.24	—	16.24	99.42	—
X.	41.26	—	—	—	44.53	—	3.84	1.84	—	8.11	99.63	—
XI.	64.54	20.85	trace	—	1.86	trace	—	—	—	0.62	100.81	2.54
XII.	56.17	—	—	—	26.10	—	—	—	—	16.83	99.10	2.20‡
XIII.	44.10	24.20	—	—	25.20	—	—	—	—	5.86	99.36	—
XIV.	53.40	22.01	—	—	10.80	trace	—	—	—	13.39	99.09	—

\* Alkalis not determined. † Incl.  $\text{MnO}$  1.50,  $\text{CuO}$  1.06,  $\text{Na}_2\text{O}$  0.61.

‡ Incl.  $\text{CuO}$  0.70,  $\text{Na}_2\text{O}$  0.20.

§ Incl.  $\text{K}_2\text{O}$  11.85,  $\text{Na}_2\text{O}$  1.18.

L. J. S.

**Two New Zircon Minerals—Orvillite and Oliveiraite.**

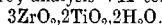
T. H. LEE (*Amer. J. Sci.*, 1919, [iv], 47, 126—132; *Revista da Sociedade Brasileira de Ciencias, Rio de Janeiro*, 1917, No. 1, 31—38).—The zirconia-bearing rock or ore ("caldasite") of the Caldas region in Minas Geraes, Brazil, consists at times mainly of baddeleyite, containing  $\text{ZrO}_2$  92%. One variety, in which the cavities are lined with small crystals of zircon, consists of a mixture of zircon and a new zirconium silicate, the latter being soluble in a mixture of hydrofluoric and hydrochloric acids. Analyses I and II are of the mixture, and III of material picked out under the microscope. The last corresponds with the formula



and for this the name *orvillite* is proposed.

	ZrO <sub>2</sub> .	SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	H <sub>2</sub> O.	Total.
I. 71-88	25.31	0.62	0.15	—	0.43	—	1.66	99.95
II. 85-01	9.63	1.52	—	3.57	—	—	—	99.73
III. 68-04	25.45	—	—	—	—	—	6.35	99.72

The second mineral—*oliveiraite*—occurs with euxenite (anal. IV) at Pomba, Minas Geraes. Most of the euxenite crystals are coated with a yellow crust (anal. V). An analysis (VI) is also given of another euxenite, from Espirito Santo, which was supposed to contain a new element. The oliveiraite is greenish-yellow with a radially fibrous structure; analysis VII corresponds with



	Ta <sub>2</sub> O <sub>5</sub> .	Cb <sub>2</sub> O <sub>5</sub> .	ZrO <sub>2</sub> .	TiO <sub>2</sub> .	UO <sub>2</sub> .
IV. 1.46	38.39		—	25.00	10.06
V.	52.51		—	25.00	4.93*
VI. 3.20	28.70		4.23	23.70	7.50
VII. —	—		63.36	29.92	—
	Ce <sub>2</sub> O <sub>3</sub> .	Y <sub>2</sub> O <sub>3</sub> .	PbO.	H <sub>2</sub> O.	Total.
IV. 0.46	23.08		0.14	2.41	99.00
V.	7.40		—	11.14	100.98
VI. —	23.12		0.14	6.41	100.12†
VII. —	—		—	6.48	99.76

\* UO<sub>3</sub>.

† Including iron oxide 3.12, SnO<sub>2</sub> trace.

L. J. S.

## Analytical Chemistry.

**Approximation in the Calculation of Chemical Analyses.**

G. PANEBIANCO (*Gazzetta*, 1918, 48, ii, 189—206).—Independently of experimental errors, the accuracy of analytical results is limited to two or three figures by the fact that the atomic weights of the

elements are exact to at most four, and more usually only three, figures. Various examples are considered, the values taken for the atomic weights and their absolute errors being those of the international table for 1911. Since  $Sb=120.2$  and  $S=32.07$ , the percentages of these two elements in antimonite are  $71.417$  and  $28.582$  respectively. If, however, the values  $120.2 \pm 0.3$  and  $32.07 \pm 0.01$  are employed in the calculation, the limiting percentages for the antimony are  $71.730$  and  $71.106$ , the absolute error being  $0.5$  ( $71.730-71.106$ ); similarly, for the sulphur, the absolute error is  $0.06\%$ . Hence the percentage of antimony is accurate to only two figures, namely,  $71$ , and that of sulphur to three figures, namely,  $28.5$ .

The relative error,  $E$ , of an atomic or molecular weight may be expressed in the form of a fraction with  $1$  as numerator and some multiple of a power of  $10$  as denominator, that is,  $1/h \cdot 10^p$ . If, then, the value of this fraction is known relatively to an approximate number, of which the first significant number to the left is  $p$ , this number will have  $n$  figures exact if  $h$  is equal to or less than  $p$ , or  $(n+1)$  figures exact if  $h$  is greater than  $p$ . Thus, for antimony with the atomic weight  $120.2$  and an absolute error  $e$  equal to  $0.3$ ,  $E < 1/4 \cdot 10^2$ ; for antimony trisulphide,  $E < (2 \times 0.3 + 3 \times 0.1)/(2Sb + 3S) = 0.63/333.61 < 1/5 \cdot 10^2$ . Further,

$$\text{for } 100 \, 2Sb/(2Sb + 3S), E_1 < E_2 + E = \\ 1/4 \cdot 10^2 + 1/5 \cdot 10^2 = 9/20 \cdot 1/10^2 < 1/2 \cdot 10^2,$$

and since  $100 \, 2Sb/(2Sb + 3S) = 71.417$  and  $2$  is less than  $7$ , only two digits, namely,  $71$ , are accurate; similarly, for the percentage of sulphur, three digits are accurate.

A table is given showing for the atomic weights of the elements the absolute and relative errors. None of the latter is greater than  $1/10^2$ , and since for a compound the relative error must be less than the greatest of the relative errors of its constituent elements, such relative error of the molecular weight may be less than  $1/10^2$ .

The number of accurate digits in the percentages of the constituent elements of a compound may be rapidly established without calculation by application of the rule stating that the number of accurate digits of a quotient or product is one less than that of the term with the least number of accurate digits. Since no atomic weight has more than four digits exact, the percentage of any element or group of elements in a compound cannot have more than three digits accurate; further, such percentage cannot have less than two digits accurate (see above).

These considerations are extended by taking into account the weight of substance taken for analysis and the sensitiveness of the balance, the calculation of the error being employed to determine the minimum quantity of substance necessary to give the maximum accuracy in the digits of the percentage composition. T. H. P.

**The Estimation of Solutions of Hydrochloric Acid and of Ammonia by Weighing Ammonium Chloride, and the Volatilisation of this Salt at Different Temperatures.**

VICTOR AUGER (*Bull. Soc. chim.*, 1918, [iv], 23, 467—472).—A reply to Villiers (compare A., 1918, ii, 332). W. G.

**Estimation of Phosphorus and Silicon in Cast Iron.**

ALFREDO CAVAZZI (*Annali Chim. Appl.*, 1918, 10, 137—149).—The method of estimating phosphorus in cast iron (A., 1917, ii, 540) has been simplified in many of its details. The mixture of ferric sulphate with silica and carbon, separated as described, is boiled for about thirty minutes with dilute nitric acid (1:5) in a beaker over which is placed a retort containing cold water to act as a reflux condenser. The solution of ferric sulphate is filtered, the residue washed with water, acidified with nitric acid, and the orthophosphoric acid in the filtrate precipitated by means of ammonium molybdate. The precipitate is washed, dissolved, reprecipitated, and dissolved in ammonia solution, as described in the original method, and the solution is boiled with 3 grams of sodium chloride in order to precipitate any remaining iron as ferric phosphate. The precipitate is washed with boiling sodium chloride solution and fused with alkali carbonates, the mass treated with boiling water and filtered, and the filtrate acidified with nitric acid, treated with ammonia in slight excess, and added to the main solution. The phosphoric acid is then precipitated with magnesia mixture. The silica is estimated in an aliquot portion of the residue of carbon and silica by ignition over a blowpipe flame in a platinum crucible. [See also *J. Soc. Chem. Ind.*, 1919, March.] C. A. M.

**Estimation of Arsenic in Ferro-molybdenum and other Alloys.**

O. BINDER (*Chem. Zeit.*, 1918, 42, 619).—The estimation of arsenic in ferro-molybdenum and similar alloys may be accelerated by carrying out all the operations in a long-necked Kjeldahl flask. The alloy is dissolved in nitric acid, the solution heated with sulphuric acid until acid fumes no longer appear, and then diluted, and the arsenic distilled from the same flask in the form of arsenious chloride. C. A. M.

**Accurate Estimation of Carbon Monoxide in Gas Mixtures.**

J. IVOR GRAHAM (*J. Soc. Chem. Ind.*, 1919, 38, 10—14r).—The author's experiments show that methods of estimation of carbon monoxide based on the reaction  $5\text{CO} + \text{I}_2\text{O}_5 = 5\text{CO}_2 + \text{I}_2$  are capable of yielding exceedingly accurate results if certain precautions are observed. Two modes of procedure are adopted for the routine estimation of this gas, according as (a) the carbon monoxide content exceeds 0.2%, and an accuracy of 0.02% is sufficient, or (b) the carbon monoxide content is about, or less than, 0.2% and a greater degree of accuracy than 0.02% is required. For the



analysis of samples as under (a), the apparatus described by the author and Winnill (T., 1914, 105, 1996) is modified, mainly by replacing the beaker of water used for heating purposes by a small steam-bath, all burette readings being taken with the U-tube at the constant temperature of the steam-bath. Descriptions and sketches are given of the apparatus and of a portable form capable of estimating very much smaller quantities of carbon monoxide accurately to within less than 0.01%. The latter apparatus is varied slightly according as it is to be used in safety pits or in "naked-light" pits or other places.

T. H. P.

**Rapid Organic Combustions of Substances containing Nitrogen.** HARRY L. FISHER and A. H. WRIGHT (*J. Amer. Chem. Soc.*, 1918, 40, 868—869).—Reimer (A., 1915, ii, 578) has used cerium dioxide as a catalyst in the combustion of organic substances; cupric oxide is also employed, and, by the addition of lead peroxide and minium, carbon and hydrogen can be estimated in substances containing nitrogen. To prevent formation of cupric nitrate, the layer of cupric oxide must be maintained at a dull red heat; the lead peroxide-minium mixture is placed in the combustion tube about 5 cm. beyond the cupric oxide, and is heated at 300—320°. Several successive combustions may then be made in the same tube without changing the cupric oxide.

W. P. S.

**Methods of Water Analysis.** ATILIO A. BADO, VICTOR J. BERNAOLA, AURELIO F. MAZZA, and LEOPOLDO DASSO (*Obras Sanitarias de la Nación, Buenos Aires*, 1918, 98 pp.).—A monograph giving a detailed account of the chemical and microbiological analytical methods in use in the Laboratorio de Análisis de Aguas y Ensayos de Materiales de las Obras Sanitarias de la Nación of Buenos Aires for the examination of potable waters.

W. S. M.

**Rapid Method of Reduction of Potassium Platinichloride.** HORSCH (*Compt. rend.*, 1919, 168, 167—169).—In the estimation of potassium, the precipitate of potassium platinichloride, after being well washed with 80% alcohol, is dissolved in boiling water and the solution transferred to a weighed platinum crucible. Two to three c.c. of alcohol are added, and the whole heated on a rapidly boiling water-bath for twenty-five minutes, after which a few more drops of alcohol are added and the heating continued for five minutes. In this way, the platinum is deposited gradually and uniformly on the interior surface of the crucible, and is quite adherent. The liquid is poured out, the deposit washed with water, and the crucible is dried, ignited, and weighed. During the ignition, the deposit turns from black to a shiny, metallic appearance, and remains adherent. For the process, it is essential to use a platinum crucible, as the reduction only takes place in the presence of platinum, and the concentration of the potassium platinichloride solution must not exceed 0.25—0.30%.

W. G.

**Gravimetric Analysis. IX.—XI. Estimation of Calcium in the Presence of Phosphoric, Arsenic, and Boric Acids.**

L. W. WINKLER (*Zeitsch. angew. Chem.*, 1919, 32, i, 24).—Calcium is precipitated quantitatively as oxalate in solutions containing phosphoric, arsenic, and boric acids provided the solution is hot and that acetic acid and ammonium chloride are present. The following procedure is recommended. About 50 c.c. of solution, containing not more than 0.1 gram of calcium, are made slightly alkaline by the addition of ammonia, drop by drop. The solution is diluted to 100 c.c., and 3 grams of ammonium chloride added and allowed to dissolve; the solution is then acidified with 10 c.c. of *N*-acetic acid, and the calcium is precipitated as oxalate as prescribed for the pure solution. The last traces of precipitate may be removed from the beaker by means of a little pure methyl or ethyl alcohol, which is then poured on to the edges of the filter so as to wash them. The result may be corrected by a blank using a pure calcium salt. If a considerable portion of arsenic or phosphoric acid is present, a double precipitation is desirable, the first precipitate being allowed to remain overnight, collected, washed with ammonium oxalate solution, ignited, the residue dissolved in hydrochloric acid, and the calcium oxalate reprecipitated as before.

A. B. S.

**Rapid Estimation of Lead in Brass and Alloys. G. H.**

HONGSON (*Chem. News*, 1919, 118, 37—38).—A gravimetric and a volumetric method for the rapid estimation of lead in brass and similar alloys are described. The gravimetric method consists in precipitation of the lead as chromate from an acetic acid solution, conversion into sulphate, and finally weighing as molybdate. Five grams of the alloy are dissolved in 25 c.c. of nitric acid (D 1.4), the solution diluted with 200 c.c. of water, and sufficient aqueous ammonia (20 c.c., D 0.880) added to precipitate all the copper. Sufficient 80% acetic acid is then added to produce a clear, slightly acid solution, and 10 c.c. of 3% potassium dichromate are added, the mixture shaken, and kept for one hour. The precipitated lead chromate is filtered on a paper pulp pad and washed to remove the copper; hot douches of 30% sulphuric acid are poured on to the pad until the precipitate is entirely white. The sulphate is then washed with water. The lead sulphate is now dissolved by pouring about 40 c.c. of hot ammonium acetate solution containing acetic acid through the filter. The solution is raised to the boiling point and treated with ammonium molybdate. The precipitate is allowed to settle, filtered through an ashless paper pad, washed with water containing a little ammonium acetate, ignited, and weighed as lead molybdate. The whole process may be completed in four hours. The volumetric process consists in precipitation of the lead as chromate, as described above; the chromate precipitate is washed with water and warm dilute acetic acid (5%) until free from copper and the excess of potassium chromate. The chromate is dissolved by pouring 1:4 hydrochloric acid on to the

precipitate, and the pad finally washed with water to wash all chromic acid through. The free chromic acid may be estimated by titration with  $N/10$ -ferrous ammonium sulphate solution or by adding 10 c.c. of 10% potassium iodide solution and titrating the liberated iodine with  $N/10$ -sodium thiosulphate solution. The whole process may be carried out in two hours. Both methods have been compared with the gravimetric sulphate method, and found to give results in excellent agreement with those obtained by the better known method.

J. F. S.

**Unification of Methods for the Analysis of Cast Iron and Steel.** A. MARINOT (*Ann. Chim. anal.*, 1919, [ii], 1, 5—10).—The following methods are suggested as being trustworthy. Total carbon may be estimated by Wiborg's method (combustion with sulphuric acid and chromic acid), by the ordinary method of combustion, or by the method described by Mahler and Goutal (*A.*, 1912, ii, 807). Manganese is estimated by Traver's method (*A.*, 1917, ii, 511), and phosphorus by the molybdate method. Sulphur is liberated as hydrogen sulphide in an atmosphere of carbon dioxide, collected in zinc acetate solution, and estimated iodometrically. Arsenic is also estimated iodometrically after distillation. [See, further, *J. Soc. Chem. Ind.*, March.] W. P. S.

**Direct Estimation of combined Ferric Oxide in Silicates Insoluble in Acids.** O. HACKL (*Chem. Zeit.*, 1919, 43, 9).—Knecht's volumetric method of estimating ferric salts by titration with titanous chloride, using potassium thiocyanate as indicator, is not directly applicable to silicates which have been decomposed with hydrofluoric acid. The influence of a small amount of this acid in preventing the appearance of the colour reaction with thiocyanate may be obviated by dissolving boric acid in the solution. This also restores the colour of ferric thiocyanate which has been destroyed by hydrofluoric acid; or methylene-blue, the colour of which is not affected by traces of hydrofluoric acid, may be used as indicator in place of potassium thiocyanate.

C. A. M.

**Estimation of Molybdenum.** KUNO WOLF (*Zeitsch. angew. Chem.*, 1918, 31, i, 140).—When molybdenum is separated as its sulphide, and the latter then converted by ignition into molybdenum trioxide and weighed, the temperature during the ignition should not exceed  $425^{\circ}$ . The conversion of the sulphide into trioxide is complete at  $400^{\circ}$ ; no further change takes place between  $400^{\circ}$  and  $450^{\circ}$ , but above  $450^{\circ}$  the trioxide sublimes. The correct temperature ( $400$ — $425^{\circ}$ ) is most readily attained by using an electric furnace.

W. P. S.

**Emanation Method of Estimating Thorium.** G. H. CARTLEDGE (*J. Amer. Chem. Soc.*, 1919, 41, 42—50).—It is shown by circulating a current of air through a thorium solution and an ionisation chamber until the activity has become constant

that the thorium content of any substance, which can be dissolved completely, may be estimated with an error which is not greater than 1.5%. In making the determination, it is advisable to draw air through the solution for some minutes, before connecting to the ionisation chamber, for the purpose of removing any radium emanation which may be present. It is also essential that the dimensions of the apparatus used should be the same in all experiments and that the temperature should be as nearly as possible the same. The method has been tested with a specimen of monazite sand, and it is found by this method that 8.61% of thorium oxide is present, whereas the gravimetric analysis indicates 8.57%. Details are given of a method of preparing a solution of monazite for this analysis. Two notes on the gravimetric analysis of monazite are appended to the paper. Carney and Campbell (*A.*, 1914, ii, 583) use ammonium perchlorate and sulphuric acid for the destruction of the filter paper and the conversion of thorium pyrophosphate into thorium sulphate. This process may be carried out in one-half the time by using sulphuric acid and fuming nitric acid (D 1.53) instead. It is shown that the practice of using a slightly turbid, unfiltered solution of monazite in the analysis leads to high thorium results, since the titanium oxide is weighed along with the thorium.

J. F. S.

#### Estimation of Gold, especially in Animal Tissues.

SIDNEY M. CADWELL and GLADYS LEAVELL (*J. Amer. Chem. Soc.*, 1919, 41, 1—12).—With the object of finding a method capable of estimating the amount of gold present in tissues, the authors have investigated the methods available for the estimation of gold, and have devised a method which, with a maximum error of 0.05 mg., is capable of estimating amounts of gold of 3.0 mg. and less. This method was required in connexion with the gold salt treatment of tuberculosis, and consists in placing 10 grams of fresh tissue in a 300 c.c. Kjeldahl flask, adding 10 c.c. each of concentrated sulphuric and nitric acids, and digesting over a free flame until the cooled solution is colourless. Air is then blown into the flask, and the mixture again heated until the volume of solution is reduced to 2 c.c.; this procedure removes most of the sulphuric acid. One c.c. each of hydrochloric and nitric acids is then added and the mixture boiled for a few minutes, and then a further c.c. of hydrochloric acid added. The solution is cooled, diluted with 5 c.c. of water, and concentrated ammonium hydroxide added until the colour is discharged, and then an excess of 2 c.c. The mixture is boiled, and the white precipitate which forms at this point dissolved by adding 5 c.c. of concentrated hydrochloric acid and boiling for three minutes. The solution is filtered through asbestos on an alundum plate, and the filtrate treated with ammonium hydroxide until it smells distinctly of ammonia. The volume of the solution should be now about 40 c.c.; 1.1 c.c. of 85% phosphoric acid and 0.75 gram of disodium hydrogen phosphate are added, and the solution electrolysed. A rotating anode and a cathode of

platinum sheet are used. The difference of electrode potential should be 0.9–1.2 volts, and the most efficient temperature is 60°. The method has been slightly modified to allow of its use for larger quantities of gold. By the addition of 6 grams of ammonium chloride to prevent precipitation, 30 to 40 mg. of gold can be electrolysed at 60°, with a voltage of less than 0.6 volt for the first thirty to forty-five minutes and below 1.3 volts for the remainder of the time, complete deposition usually requiring one and a-half hours. Under the conditions stated, gold can be completely separated from equivalent amounts of copper and iron, but the time required for electrolysis is greater than when these substances are not present. It makes very little difference whether the electrolysed solution is neutral or much more acid than stated above. The average time required for carrying out a complete analysis of gold by this method is less than two hours. J. F. S.

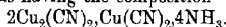
**Quantitative Estimation of Sugar. A New Apparatus for the Estimation of Sugar in Urine.** H. CITRON (*Munch. med. Woch.*, 1918, 65, 1053; from *Chem. Zentr.*, 1918, ii, 869).—The author describes a simple apparatus for the estimation of sugar in urine according to Bang's method. H. W.

**Quantitative Colorimetric Estimation of Pentosans in Meal.** G. TESTONI (*Staz. sper. agr. Ital.*, 1917, 50, 97–108; from *Chem. Zentr.*, 1918, ii, 865–866).—The method of Tollens and Krueger gives high results, because the starch is slowly but continuously converted into furfuraldehyde. Sucrose, maltose, and dextrose when heated with hydrochloric acid of the prescribed concentration also yield distillates from which phloroglucides are obtained. The hexoses, starch, and cellulose cause incorrect results in the estimation of methylpentosans, since, when treated with dilute mineral acid, they give, as intermediate product,  $\omega$ -hydroxy-methylfurfuraldehyde, which yields a phloroglucide, m. p. 95°, soluble in alcohol.

The author has therefore endeavoured to find a process by which the pentosans can be converted into pentoses easily identified by colour reactions, whilst the other constituents of the meal are not attacked in a vitiating manner. The most suitable reagent is a mixture of acetic acid (90 c.c.) and concentrated hydrochloric acid (D 1.19, 10 c.c.) at 45–50°. On addition of 0.25% phloroglucinol to this mixture, a red solution is obtained, which remains clear even when diluted with one hundred times its volume of water, and has well-marked absorption bands in the red, yellow, and blue. Different varieties of starch, dextrins, and different sugars have no influence on the reaction, whilst pentoses alone and in artificial mixtures are quantitatively found. The pentosans, even those contained in clover, are completely hydrolysed when heated for forty-five minutes with the reagent. H. W.

**Action of Potassium Cyanide on Ammoniacal Copper Sulphate and its Application to the Estimation of Hydrocyanic Acid and Copper.** L. JENNESSEUX (*Ann. Chim. anal.*, 1919, [ii], 1, 15–20).—Lassaigne's test for hydrocyanic acid (form-

ation of a white precipitate when a cyanide solution is treated with a drop of copper sulphate solution, then with sodium hydroxide solution, and the mixture acidified with sulphuric acid) may be rendered more sensitive if the copper sulphate solution is first treated with sodium hydrogen sulphite in quantity sufficient to change the colour from blue to green. When potassium cyanide solution is added to ammoniacal copper sulphate solution, a crystalline precipitate forms having the composition



Further addition of cyanide then causes the solution to become colourless, and the precipitate dissolves. This point is reached when a definite proportion of cyanide has been added, and the reaction may be used for the estimation of hydrocyanic acid, and, conversely, of copper. The copper sulphate solution used should contain 4.99 grams of the crystallised salt per 100 c.c., and this solution is mixed with 80 c.c. of *N*/1-ammonia and 20 c.c. of water; 10 c.c. of the mixture is a convenient quantity to take for an estimation. [See, further, *J. Soc. Chem. Ind.*, 1919, March.]

W. F. S.

**Opium Analysis.** D. B. DOTT (*Pharm. J.*, 1918, 101, 318).—The author deals with certain criticisms by Annett and Singh (*A.*, 1918, ii, 279) on the British Pharmacopœia method for the assay of opium by the lime-water process. Whatever may be the solvent influence of codeine on morphine in aqueous solution, the conditions of the assay process are entirely different, in that sufficient ether is added to hold in solution all the codeine possibly present. Moreover, the author has checked the alternative method proposed (*loc. cit.*), consisting in shaking the lime-water solution of the alkaloids with toluene to remove the codeine before precipitating the morphine by the official process. This alternative method (using benzene instead of toluene) gave a morphine precipitate heavier in weight and showing a higher titration value, but obviously less pure than the morphine prepared by the standard method. When the impurities were removed by washing with 80% alcohol saturated with morphine, the morphine prepared by the new process was no more than that prepared by the Pharmacopœia process, and there is no reason for altering the latter in the direction indicated by Annett and Singh.

J. F. B.

**Separation and Estimation of Uric Acid and other Purines in Urine.** F. TELLE (*Bull. Sci. Pharmacol.*, 1918, 25, 208—211; from *Chem. Zentr.*, 1918, ii, 770).—The uric acid is precipitated by the addition of solid ammonium chloride and ammonia to the acid urine, and, after collecting on a small filter, estimated by titration with permanganate in the presence of sulphuric acid. The purines in the filtrate are estimated by Denigès's method.

H. W. B.

**Quick Estimation of Albumin (in Urine).** A. SIMON and C. PAGEL (*Bull. Sci. Pharmacol.*, 1918, 25, 204—208; from *Chem. Zentr.*, 1918, ii, 767).—The urine is treated with saturated sodium

sulphate solution and two or three drops of acetic acid, and is then heated until the albumin separates in flocks. By means of the diaphanometer described in the original paper, the height of the liquid is determined at which a line drawn on the bottom of the vessel is no longer discernible. The amount of albumin in the urine can then be read off from the accompanying table. H. W. B.

**Estimation of Urobilin in Urine.** S. MARCUSSEN and SVEND HANSEN (*J. Biol. Chem.*, 1918, **36**, 381—389).—The presence of urobilin in urine may be readily detected by the following modification of Schlesinger's test. One gram of zinc acetate is weighed into a test-tube, and 10 c.c. of absolute alcohol are then added; 10 c.c. of the urine are placed in another test-tube, to which are added three drops of a 5% alcoholic solution of iodine. The contents of the two test-tubes are then mixed by repeated decantations until all the zinc acetate has dissolved. After filtering off the precipitate, the filtrate is found to be fluorescent if urobilin or urobilinogen was originally present in the urine.

By diluting the urine until fluorescence is no longer obtainable, a rough idea is furnished of the quantitative relationship of the urobilin.

H. W. B.

**The Estimation of the Nuclein Content of Yeast.** C. A. LUBSEN (*Pharm. Weekblad*, 1918, **55**, (50), 1625—1628).—The hydrolysis of nucleoproteins by hydrochloric acid-pepsin solutions yields soluble albumins and an insoluble residue of nucleins; the latter contain 4—7% of phosphoric acid, representing the whole of the phosphorus present in the nucleoprotein. Further hydrolysis, for example, by trypsin, yields another albumin group, together with a nucleic acid. In analysing foodstuffs for nuclein content, Jebbink employs the pepsin-hydrochloric acid hydrolysis, using a solution containing 0.24% HCl, and determines the phosphorus in the insoluble residue of nuclein, using this as a measure of the nuclein content. Grijns criticises this method on the ground that so strong a solution of hydrochloric acid would cause further hydrolysis of the nuclein to the soluble nucleic acid, thus leading to low results.

The author has examined the question by carrying out experiments with yeast, using pepsin-hydrochloric acid solutions containing various proportions of hydrogen chloride. He finds that the weak solution (0.1% HCl) recommended by Grijns gives low results, owing to the slowness of the hydrolysis, whereas Jebbink's solution (0.24% HCl), and even stronger solutions (0.35% HCl), gives accurate results. It is therefore clear that the nucleins are not further hydrolysed by acid solutions of this strength, and Grijns's contention appears to have been wrongly based on the assumption that hydrolysis proceeded to the soluble nucleic acids. S. I. L.

